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THE FIRE RESISTANT TREATMENT OF TEXTILES

FINAL REPORT

February 1, 1953 -- June 3, 1955

Research and Development Command

Office of the Quartermaster General

Contract No. DA44-109-qm-1414

Project No. 7-92-06-001

Department of Chemistry  
University of Rhode Island  
Kingston, Rhode Island

Morton H. Gollis  
Frank R. Fisher

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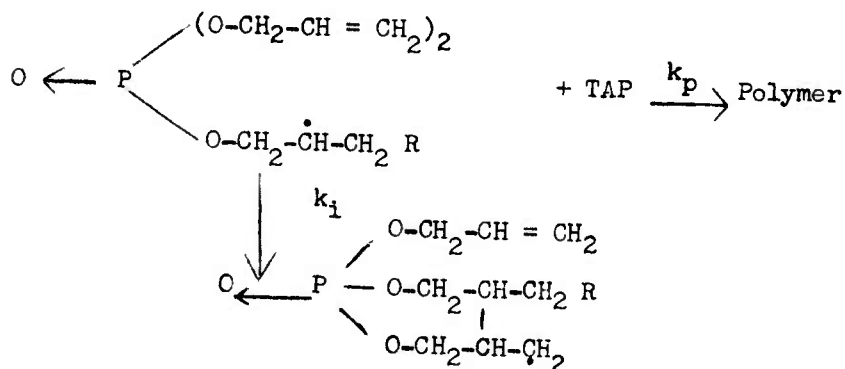
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### Compound Development

During the period covered by this report research was continued to develop satisfactory flame-retardant treatments for cotton fabric. Primarily, these investigations involved the continued study of the polymerization of triallyl phosphate under various conditions and evaluation of the products obtained. In addition, the synthesis and screening of other compounds, especially organophosphorus compounds, were continued.

### Kinetics of Solution Polymerization of Triallyl Phosphate.

The study of the benzoyl peroxide initiated solution polymerization of triallyl phosphate has been completed. The rate of intramolecular reaction was investigated by determining the iodine number (available double bonds) in the polymerization of different concentrations of the phosphate in  $\beta, \beta'$ -dichloroethyl ether and extrapolating to zero time.



$$\text{Rate of propagation} = r_1 = k_p [\text{R}\cdot] [\text{M}]$$

$$\text{Rate of intramolecular reaction} = r_2 = k_i [\text{R}\cdot]$$

$$\frac{r_1}{r_2} = \frac{k_p [\text{M}]}{k_i}$$

The results obtained at different concentrations are illustrated by the expected straight line in Figure 1. The ratio of  $k_i/k_p$  was determined to be 0.09.

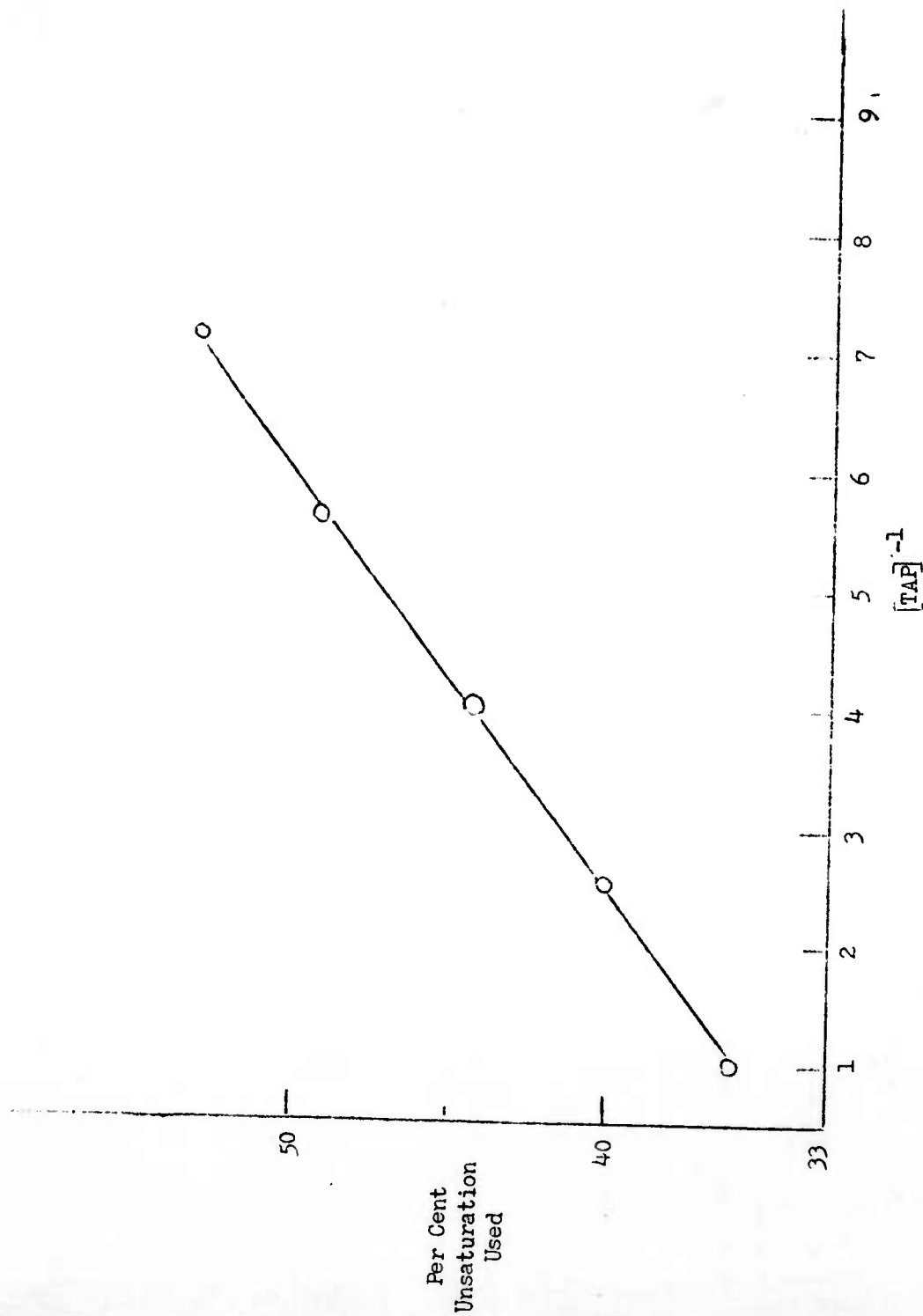


Figure 1. Polymerization of triallyl phosphate in  $\beta, \beta'$ -dichlorethyl ether at 100° C.

Bromoform - Triallyl Phosphate Emulsion Polymer.

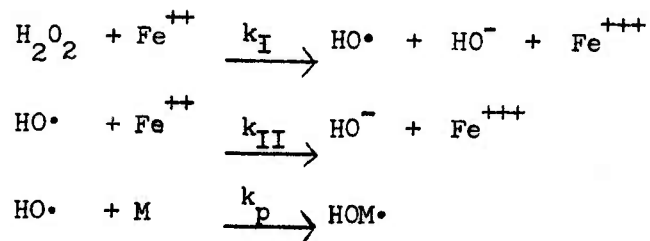
Supplemental studies on the bromoform - triallyl phosphate emulsion polymer, developed by the Southern Regional Research Laboratory, were concluded. A method for characterizing the polymer, which has proved less time-consuming than the sol/gel ratio method, was developed. The procedure involved the determination of the methanol-insoluble fraction of the emulsion at different reaction times.

The change in density of the emulsion during the polymerization was determined. A three per cent increase was observed. This increase was sufficiently great that the course of the polymerization could be followed and controlled. Figure 2 illustrates the density change and weight of methanol-insoluble fraction as a function of time for a successful and unsuccessful experiment.

The retention to laundering of cotton khaki fabric treated with the emulsion polymer was determined. The average per cent of retention after one laundering of ten samples of fabric with different amounts of add-on was  $80 \pm 2$  per cent.

Thirty experiments with different redox conditions were unsuccessful in the polymerization of bromoform-triallyl phosphate. Hydrogen peroxide, potassium persulfate, benzoyl peroxide and cumene hydroperoxide were used as initiators with ferrous sulfate as the reducing agent and sodium pyrophosphate as the complexing agent. In some experiments sorbose was used to regenerate the ferrous ion. In such a redox polymerization competition between the free radical oxidation of ferrous ion and the addition of monomer occurs as follows:





In the polymerization of methol acrylate<sup>1</sup>

$$k_p / k_{II} = 0.2$$

Allyl polymerization is much slower and requires a higher peroxide concentration with both reactions favoring the oxidation of ferrous ion. The presence of bromoform would make a successful redox system even more unlikely.

Preliminary experiments were completed on the emulsion polymerization of triallyl phosphate-bromoform with added silicon compounds to improve the durability and water repellency of treated fabric. The silicon compounds investigated were vinyltriethoxysilane and sodium silicate. The emulsions obtained padded very poorly and the durability of the treated fabric to laundering was not improved. This investigation was discontinued.

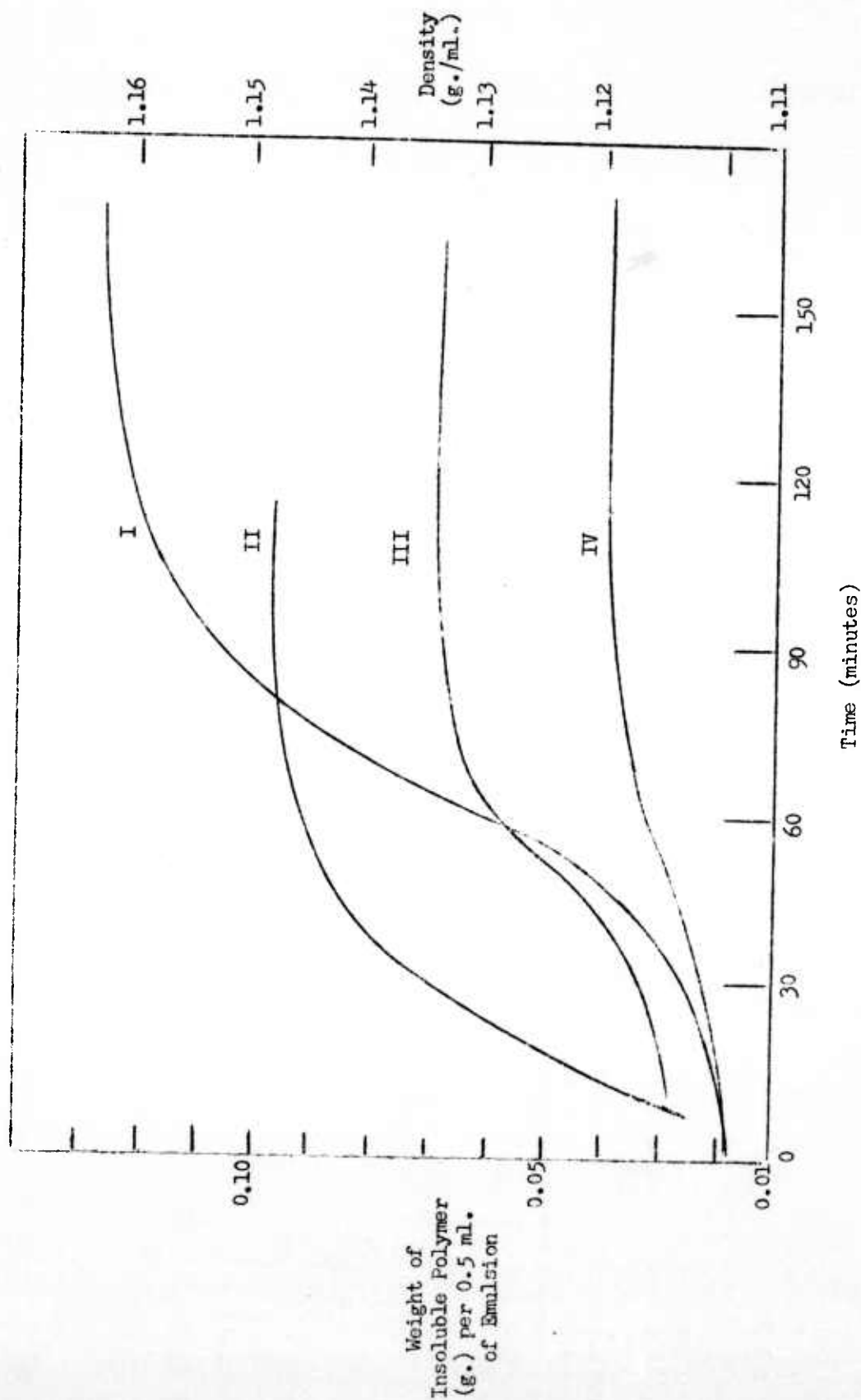


Figure 2. Variation of density and insoluble polymer with time. Insoluble polymer (I) and density (II) for an emulsion provided durability and insoluble polymer (IV) and density (III) for an unsuccessful emulsion.

Polymerization of Triallyl Phosphate in Chloroform.

From previous work on flame retardants the Southern Regional Research Laboratory proposed that the incorporation of halogen in an organic flame retardant treatment for cotton fabric reduced the flammability of the volatile tars produced during thermal decomposition of the fabric.<sup>2</sup> The moderate success of brominated triallyl phosphate as a flame retardant encouraged this laboratory to investigate various means of incorporating halogen in polymerized triallyl phosphate.

The free radical initiated polymerization of triallyl phosphate in chloroform solution was studied in an attempt to incorporate halogen in the polymer by a chain transfer process. The phosphate was polymerized in an equal weight of chloroform using an amount of benzoyl peroxide equal to one per cent of the weight of the reactants. The reaction was stopped when a threefold increase in relative viscosity was obtained. The change in relative viscosity, reaction mixture temperature and per cent of conversion with reaction time for a typical experiment are given in Figure 3a, 3b, and 3c. The chlorine content of the powdered polymer was approximately two per cent.

Samples of ethylene dichloride solutions of the polymer were submitted to the Textile Functional Finishes Laboratory, Research and Development Command, Quartermaster Corps, for evaluation. The fire resistance characteristics of cotton khaki fabric with a 16% add-on were satisfactory. However, a marked reduction (approximately 60 per cent) in tear strength was observed. This loss was not restored by the use of Paraplex AL-III plasticizer. A summary of the evaluation report appears in the following table.

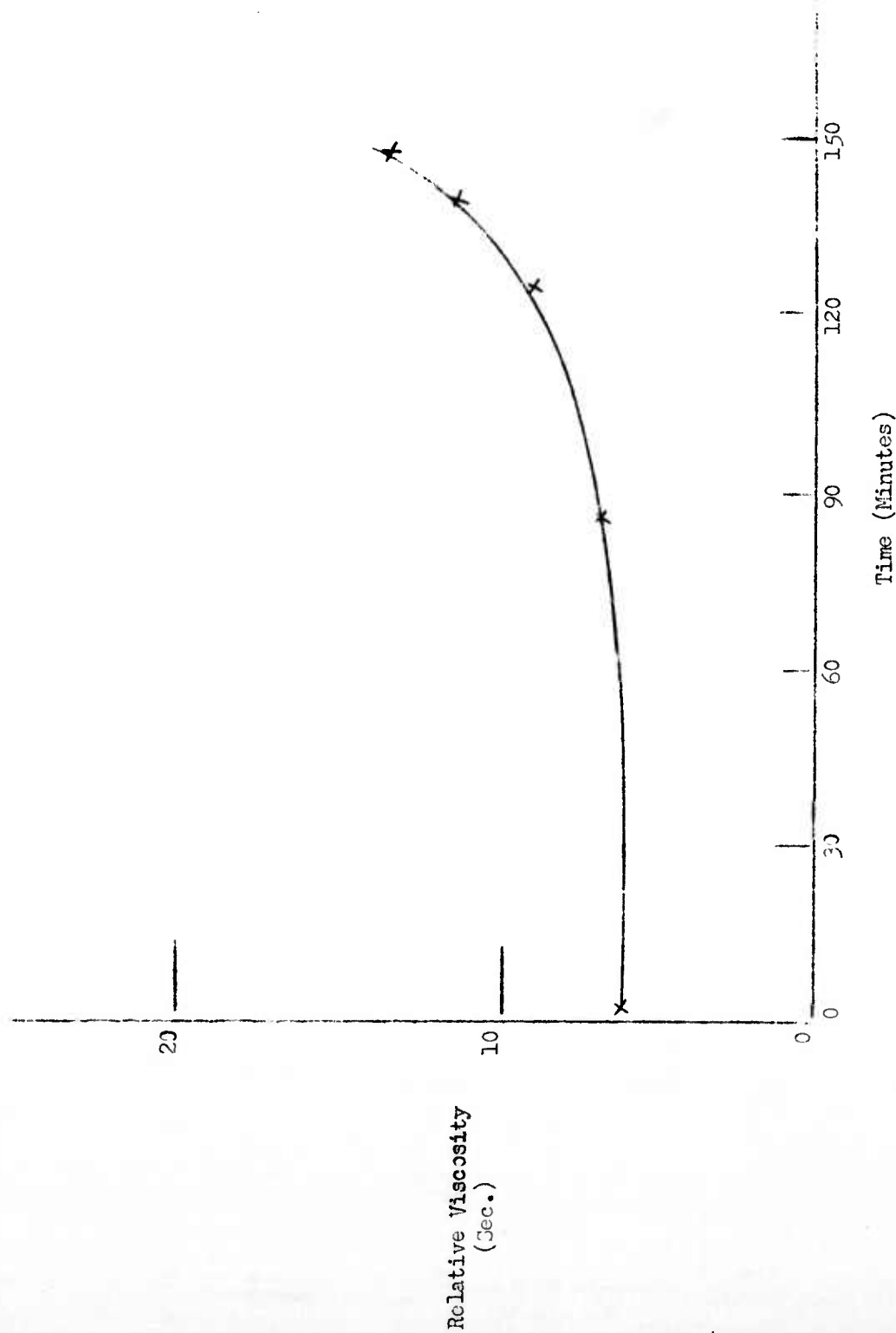


Figure 3a. Change in viscosity with time in the polymerization of triallyl phosphate in chloroform.

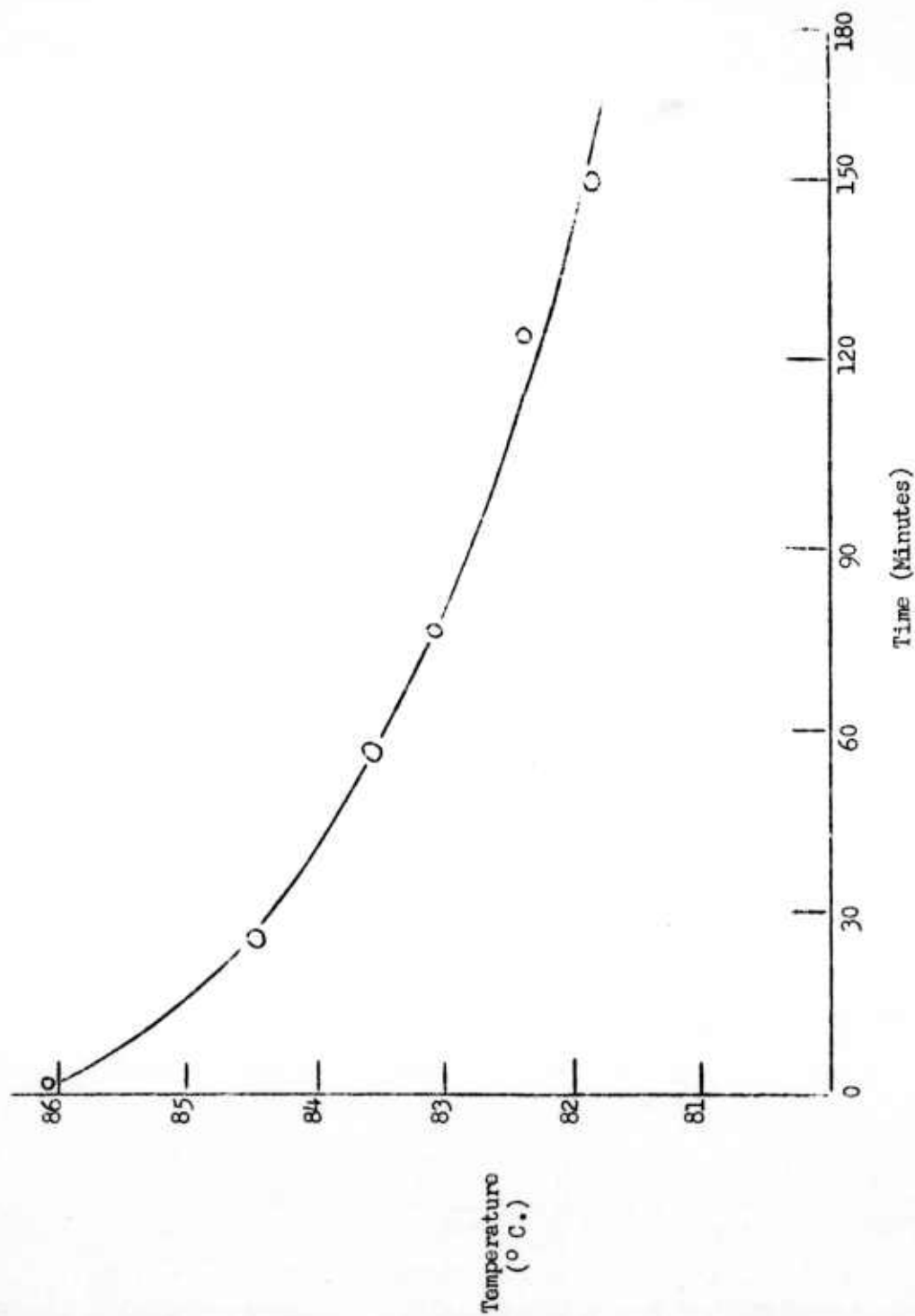


Figure 3b. Variation in reaction mixture temperature with time in the polymerization of triallyl phosphate in chloroform.

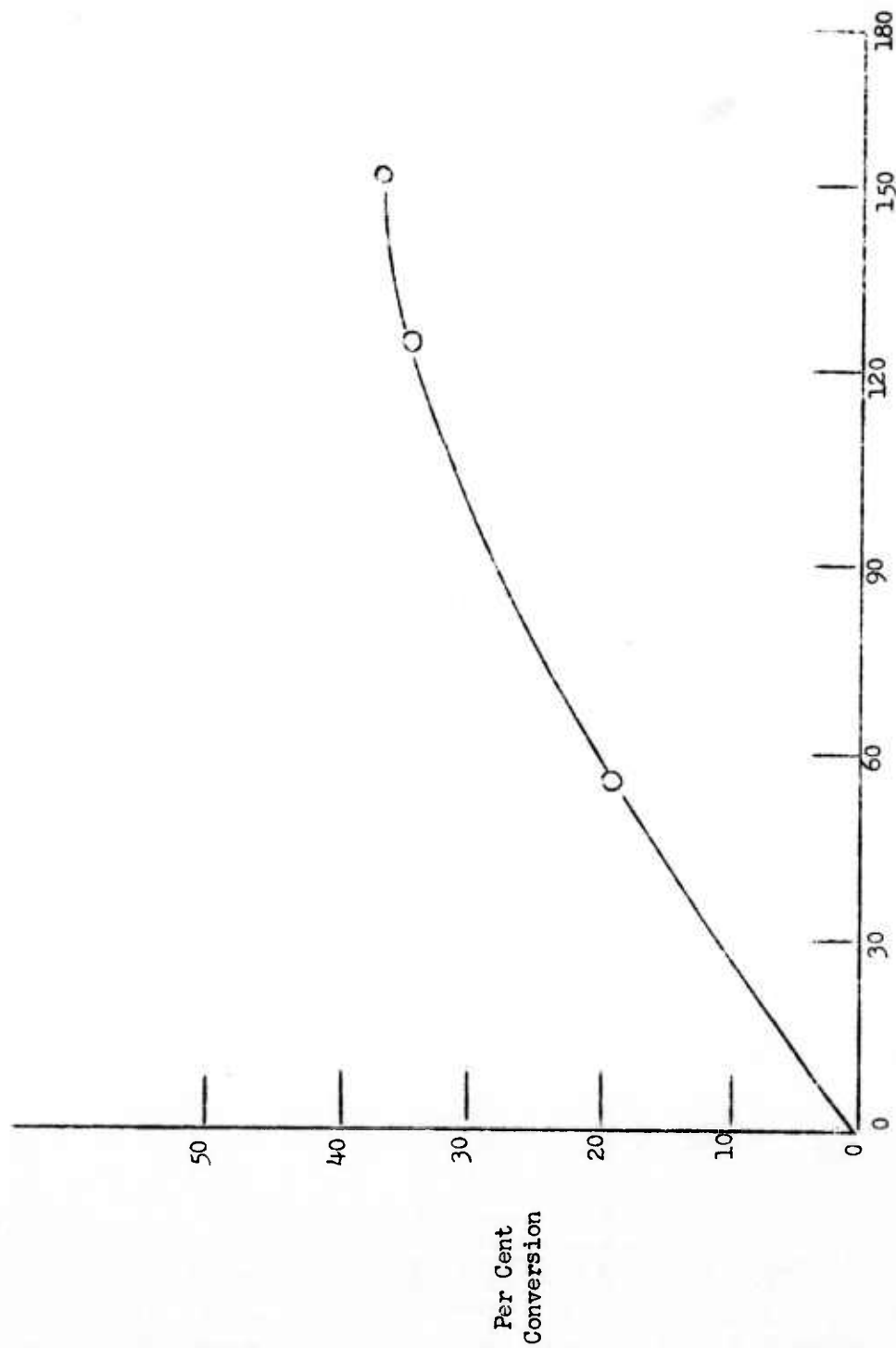


Figure 3c. Variation in conversion with time in the polymerization of triallyl phosphate in chloroform.

TABLE I

Evaluation of Triallyl Phosphate - Chloroform Polymer

| <u>Polymer</u>                   | <u>Add-on %</u> |                       | <u>Laundry Cycles</u> |          |          |          |           |
|----------------------------------|-----------------|-----------------------|-----------------------|----------|----------|----------|-----------|
|                                  |                 |                       | <u>0</u>              | <u>1</u> | <u>6</u> | <u>9</u> | <u>15</u> |
| TAP-CHCl <sub>3</sub><br>(RI-18) | 16%             | Afterflame,<br>(sec.) | 0                     | 0        | 0        | 0        | 0         |
|                                  |                 | Afterglow,<br>(sec.)  | 2.0                   | 2.0      | 3.0      | 3.0      | 4.0       |
|                                  |                 | Char Length,<br>(in.) | 4.2                   | 4.2      | 4.1      | 4.2      | 5.1       |

Cotton khaki fabric treated with a 21 per cent add-on of the polymer also possessed satisfactory fire-resistant properties; however, the treated sample burned when a match flame was applied. An improvement in flexibility and tear strength was obtained by working the treated fabric with a detergent and treating with a softener. The following table summarizes the results of the evaluation.

TABLE II

Evaluation of Triallyl Phosphate - Chloroform Polymer

| <u>Polymer</u>                    | <u>Add-on %</u> |                      | <u>Laundry Cycles</u> |          |          |           |
|-----------------------------------|-----------------|----------------------|-----------------------|----------|----------|-----------|
|                                   |                 |                      | <u>0</u>              | <u>1</u> | <u>9</u> | <u>15</u> |
| TAP-CHCl <sub>3</sub><br>(RI-19B) | 21%             | Afterflame<br>(sec.) | 0                     | 0        | 0        | 0         |
|                                   |                 | Afterglow<br>(sec.)  | 2                     | 2        | 2        | 2         |
|                                   |                 | Char length<br>(in.) | 4.1                   | 4.0      | 3.8      | 3.7       |

Modification of the polymer was studied to improve the properties of the treated fabric (flexibility, tear strength, etc.). The polymer samples evaluated as indicated in Tables I and II, consisted of higher molecular weight fractions obtained by repeated washing of the reaction mixture with petroleum ether until an amorphous solid resulted.

In one experiment the reaction mixture was precipitated with petroleum ether and not washed. A gummy product containing low molecular weight fractions was obtained. In another polymerization the reaction was modified by adding five per cent by weight of carbon tetrachloride. The low molecular weight fractions were removed from the product by repeated working with petroleum ether to produce an amorphous powder. The three polymers were applied to cotton khaki fabric and evaluated. As shown in the following table, no significant improvement in tear strength was observed.

TABLE III

Modification of the Triallyl Phosphate-Chloroform  
Polymer to Improve the Tear Strength of the Treated Fabric

|  | <u>Precipitated<br/>Polymer</u> | <u>Powdered<br/>Polymer</u> | <u>Polymer Moderated<br/>with 5% CCl<sub>4</sub></u> |
|--|---------------------------------|-----------------------------|--|
| Conversion, %  | 45                              | 34                          | 38   |
| Chlorine, %  | 2.1                             | 2.1                         | 3.4  |
| Retention after 1 laundering, %                            | 95                              | 95                          | 95   |
| Vertical flame test, CL <sup>a</sup>                       | 3.3                             | 4.3                         | 4.0  |
| Vertical flame test after<br>1 laundering, CL <sup>a</sup> | 3.1                             | 3.5                         | 3.2  |
| Elmendorf tear strength                                    | 36                              | 36                          | 42   |
| Elmendorf tear strength after<br>1 laundering              | 46                              | 39                          | 42-57  |

<sup>a</sup>CL = Char Length (in.)

Triallyl phosphate was polymerized in twice the weight of chloroform to a threefold increase in original viscosity. The conversion was 52 per cent. The chlorine content of the powdered polymer was six per cent. Cotton khaki fabric treated with this polymer required a 28 per cent add-on to pass the Vertical Flame Test.



The polymerization of triallyl phosphate in an equal weight of chloroform was successfully completed on a semi-pilot plant scale. The measurement of the relative viscosity as a function of time was effective as a control measure. The reaction was continued to a threefold increase in relative viscosity. The unreacted monomer and chloroform were recovered and recycled in the polymerization. The conversion per cycle was 34-36 per cent.

Polymerization of Triallyl Phosphate in some Halomethanes.

Experiments on the benzoyl peroxide-initiated solution polymerization of triallyl phosphate in some halomethanes, as chain-transfer agents, were completed to prepare a durable flame retardant. Cotton khaki fabric treated with the products possessed a soft hand but were not effectively flame retardant.

Triallyl phosphate was polymerized in an equal weight of carbon tetrachloride until a threefold increase in original viscosity was observed.

The gummy product (45% conversion) could not be powdered and had a chlorine content of 14 per cent. Cotton khaki fabric treated with a 20 per cent add-on of the polymer was not flame resistant.

Triallyl phosphate was polymerized in an equal weight of bromochloromethane. The resulting pasty polymer (34% conversion) contained approximately two per cent halogen. Cotton khaki fabric treated with an 18 - 22 per cent add-on of the polymer was not flame resistant after two launderings.

The polymerization of triallyl phosphate in bromodichloromethane produced a gummy product which could not be powdered. The per cent conversion, based on the phosphate, was high (118%), compared to that obtained for the polymerization in chloroform (35%). The isolation of a gum in high yield suggested that the halomethane was participating in an addition reaction across the allyl group double bonds as well as a chain-transfer agent.

Kharasch and coworkers<sup>3</sup> have reported that polyhalomethanes react with olefins, containing terminal double bonds, under the influence of peroxides to form products containing one or more equivalents of the olefin to each equivalent of the halomethane. A study of the comparative reactivity of carbon tetrachloride and chloroform toward an olefin by Kharasch showed that the main product was the one-to-one addition product in high yield when carbon tetrachloride was used. A lower yield of the one-to-one addition product and a considerable amount of polymeric material was formed when chloroform was used.

The triallyl phosphate-chloroform (1:1) polymer (discussed in the preceding section of this report) and the triallyl phosphate-carbon tetrachloride (1:1) polymer, as prepared in this laboratory, had a halogen content of 1.5-2.1 per cent and 14 per cent, respectively. The former value indicated a ratio of 23-32 triallyl phosphate units per unit of chloroform in the polymer. The latter halogen percentage indicated that the triallyl phosphate-carbon tetrachloride polymer contained approximately four units of the phosphate per unit of halomethane. These results suggested that chloroform reacted principally as a chain-transfer agent whereas carbon tetrachloride added across available allyl group double bonds during the polymerization process.

From the experimental observations it appeared reasonable to expect that the polymerization of triallyl phosphate in bromochloromethanes would provide products of high halogen content and low phosphate-halomethane ratio with accompanying decrease in the number of double bonds available for cross-linking on fabric during curing processes. This reduced unsaturation would result in less durable treatments<sup>4</sup>. In addition, the treated fabrics would possess a soft hand since less complicated structures would result from the further polymerization on fabrics during curing of the polymer, containing a reduced degree of unsaturation<sup>5</sup>.

The benzoyl peroxide-induced polymerizations of triallyl phosphate in chloroform and bromodichloromethane were repeated. In addition, the reaction was carried out in bromoform, bromotrichloromethane and combinations of each bromochloromethane with chloroform. The amount of unsaturation in the products obtained was determined by the iodine number. The products were applied to cotton khaki fabric and screened for flame-retardant properties.

The polymerization of triallyl phosphate in bromodichloromethane, bromotrichloromethane and bromoform, respectively, did not produce favorable fire retardants. The products obtained possessed a higher halogen content, lower ratio of triallyl phosphate units per halomethane unit and a lower amount of available unsaturation than was observed for the triallyl phosphate-chloroform polymer. Cotton khaki fabric treated with the former products had a soft hand and exhibited poor durability to laundering. Fabric treated with the latter polymer possessed a stiff hand and relatively good durability. The results are summarized in the following tables.

TABLE IV

Solution Polymerization of Triallyl Phosphate in Some Halomethanes  
(Benzoyl Peroxide Induced)

| Reactants   | State of Product | Reaction Temp. (°C.) | Reaction Time (hr.) | Conversion % | Viscosity Increase | Iodine Number | Residual Unsaturation (%) | Halogen Content % | TAP/<br>Halomethane Unit |
|---|------------------|----------------------|---------------------|--------------|--------------------|---------------|---------------------------|-------------------|--------------------------|
| TAP (undistilled)   | Liquid           |                      |                     |              |                    | 339           |                           |                   |                          |
| TAP-CHCl <sub>3</sub> (1:1)                                   | Solid            | 90                   | 0.5                 | 40           | 4.4x               | 140           | 41                        | 1.5-2.1           | 23-32                    |
| TAP-(ClCH <sub>2</sub> CH <sub>2</sub> ) <sub>2</sub> O (1:1) | Solid            |                      |                     |              | 4x                 |               | 46                        | 1                 | 32                       |
| TAP-CCl <sub>4</sub> (1:1)                                    | Gum              |                      |                     | 45           | 3x                 |               |                           | 14.               | 4                        |
| TAP-CHBr <sub>3</sub> (1:1)                                   | Paste            | 85-100               | 7.5                 | 83           | 3x                 | 86.2          | 25                        | 36.4              | 1.9                      |
| TAP-CH <sub>2</sub> ClBr (1:1)                                | Solid            | 90                   | 0.75                | 34           | 3x                 |               |                           | 1.8               | 24                       |
| TAP-CHCl <sub>2</sub> Br-CHCl <sub>3</sub> (1:1:0.5)          | Gum              | 103                  | 0.5                 | 118          | 4.5x               | 75.1          | 22                        | 26.8              | 1.8                      |
| TAP-CHCl <sub>2</sub> Br-CHCl <sub>3</sub> (1:0.5:0.6)        | Gum              | 84                   | 1                   | 106          | 4.1x               | 107           | 32                        | 20.7              | 2.6                      |
| TAP-CCl <sub>2</sub> Br (1:1)                                 | Paste            | 85-95                | 6.5                 | 23           | 2x                 | 92.4          | 27                        |                   |                          |

TABLE V

Results of Vertical Flame Tests on Cotton Khaki Fabric Treated  
with the Products from the Solution Polymerization of Triallyl  
Phosphate in Some Halomethanes

| Product From:  | Add-on (%)                             | Hand         | AF <sup>a</sup> (sec.) | AG <sup>b</sup> (sec.) | CL <sup>c</sup> (in.) | 1 Laundering                       |           |           |                       | 2 Launderings   |           |           |                 |
|--|--|--------------|------------------------|------------------------|-----------------------|------------------------------------|-----------|-----------|-----------------------|-----------------|-----------|-----------|-----------------|
|  |  |              |                        |                        |                       | Ret. (%)                           | AF (sec.) | AG (sec.) | CL (in.)              | Ret. (%)        | AF (sec.) | AG (sec.) | CL (in.)        |
| TAP-CHCl <sub>2</sub> Br (1:1)                         | 18.4 <sup>f</sup><br>22.6 <sup>f</sup> | Soft<br>Soft | 0<br>0                 | 0<br>0                 | 5.5<br>4              | 53 <sup>f</sup><br>53 <sup>f</sup> | 16<br>28  | 0<br>0    | BE <sup>d</sup><br>BE |                 |           |           |                 |
| TAP-CHCl <sub>2</sub> Br (1:1.67)                      | 18.7 <sup>f</sup>                      | Soft         | 0                      | 0                      | 3.5                   | 70 <sup>f</sup>                    | 25        | 0         | BE                    |                 |           |           |                 |
| TAP-CHCl <sub>2</sub> Br-CHCl <sub>3</sub> (1:1:0.5)   | 19.1 <sup>f</sup>                      | Soft         | 0                      | 0                      | 3.8                   | 44 <sup>f</sup>                    | 20        | 0         | BE                    |                 |           |           |                 |
| TAP-CHCl <sub>2</sub> Br-CHCl <sub>3</sub> (1:0.5:0.6) | 17.0 <sup>f</sup>                      | Soft         | 0                      | 0                      | 5                     | 48 <sup>f</sup>                    | 21        | 0         | BE                    |                 |           |           |                 |
| TAP-CHCl <sub>2</sub> Br (1:1)<br>Brominated           | 22.2 <sup>g</sup>                      | Stiff        | 0                      | 0                      | 4.9                   | 51 <sup>f</sup>                    | 24        | 0         | BE                    |                 |           |           |                 |
| TAP-CCl <sub>3</sub> Br (1:0.5)                        | 18.0 <sup>f</sup>                      | Soft         | 0                      | 0                      | 6                     | 50 <sup>f</sup>                    | 18        | 0         | BE                    |                 |           |           |                 |
| TAP-CHBr <sub>3</sub> (1:1)                            | 23.1 <sup>f</sup>                      | Soft         | 0                      | 0                      | 2.8                   | 68 <sup>h</sup>                    | 0         | 0         | 3.5                   | 29 <sup>f</sup> | 17        | 0         | BC <sup>e</sup> |

<sup>a</sup> AF - Afterflame.

<sup>b</sup> AG - Afterglow

<sup>c</sup> CL - Char length.

<sup>d</sup> BE - Burned to end.

<sup>e</sup> BC - Burned completely.

<sup>f</sup> These Samples burned when an ignited match was applied.

<sup>g</sup> Four seconds AF when an ignited match was applied.

<sup>h</sup> No AF when an ignited match was applied.

Diallyl  $\alpha$ -Carbethoxyethyl Phosphate and Diallyl  $\beta$ -Bromoethyl Phosphate.

Diallyl  $\alpha$ -carbethoxyethyl phosphate was prepared in high yield by the interaction of phosphorus oxychloride with ethyl lactate and allyl alcohol. Experiments to polymerize the phosphate in an emulsion medium failed. Cotton khaki fabric treated with a 25 per cent add-on of this compound was not flame resistant.

Diallyl  $\beta$ -bromoethyl phosphate was prepared in high yield by the interaction of phosphorus oxychloride with ethylene bromohydrin and allyl alcohol. Experiments to polymerize this phosphate in emulsion medium failed. Cotton khaki fabric treated with a 27 per cent add-on of the compound was not flame resistant.

Miscellaneous Phosphorus - and Nitrogen-containing Compounds as Possible Flame Retardants.

The reaction of ethylene diamine with phosphorus oxychloride and phosphorus pentoxide was studied to obtain water-soluble polymers that would offer promise as flame retardants when applied with a binding resin to cotton fabric. The optimum results were obtained for the reaction of the oxychloride with an equal weight of the diamine in chloroform solution. The resulting white polymeric solid was dissolved in water and applied to cotton khaki fabric with melamine-formaldehyde resin (Aerotex M-3 resin). Upon application of the polymer with both an equal weight and double the weight of binder resin (20% and 17% total add-on, respectively) the treated fabric samples were not flame resistant after one laundering.

Polymers formed from the reaction of phosphorus oxychloride with urea, diethylene triamine and triethylene tetramine were prepared. Cotton khaki fabric treated with these products and a melamine-formaldehyde resin were not flame resistant after one laundering.

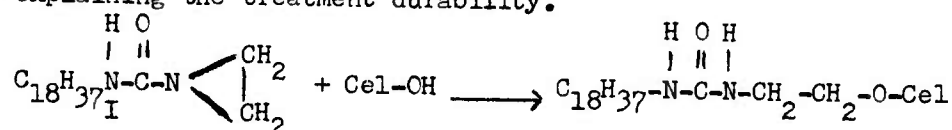
In addition, screening tests were completed on the condensation of ethylene diamine, diethylene triamine and triethylene tetramine with low molecular weight aldehydes to prepare water-insoluble polymeric flame retardants. Each of the amino compounds was treated separately with an equimolar amount of formaldehyde and glyoxal in aqueous solution. Samples of the resulting solutions were cured at 110° C. Only the mixture of diethylene triamine with formaldehyde proved promising since the cured sample was a clear, fairly hard film which was only slightly water-soluble. However, cotton khaki fabric treated with this mixture and cured was not flame resistant.

The reaction of diethylene triamine with phosphorus oxychloride in chloroform solution was investigated. The polymeric product was a near colorless, amorphous, water-soluble solid. Various mixtures of this product with melamine-formaldehyde resin and formaldehyde, respectively, were applied to cotton khaki fabric. The treatments, however, proved unsatisfactory as durable flame retardants.

The reaction of ethanolamine and phosphorus oxychloride was studied to prepare tri- $\beta$ -aminoethyl phosphate. The reaction of such a compound with formaldehyde (condensation between free amino groups of the ester and formaldehyde) suggested a possible polymeric flame retardant. However, the reaction of the sodium salt of ethanolamine with phosphorus oxychloride and the reaction of the amino alcohol itself with the oxychloride in the presence of pyridine produced only brown, resinous, water-soluble gums. The application of aqueous solutions of the products and formaldehyde by single - and double-bath techniques to cotton khaki fabric, followed by curing and leaching with water, provided a low add-on (2-5%) and failed to impart flame resistance to the fabric.

N, N', N''-Triethylenephosphoric Triamide.

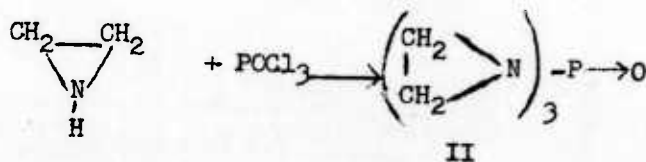
During World War II German investigators developed a durable water-repellent treatment for cotton fabric consisting of the application of N-octadecyl-N'-ethylene urea (I)<sup>6</sup>. The claim was made that this compound reacted directly with cellulose during curing, forming an ether linkage, thus explaining the treatment durability.



The incorporation of an ethyleneimine grouping in an organophosphorus compound was considered as a possibility for providing an effective permanent flame retardant for cotton fabric. The ease with which the imine ring is cleaved and condensed with a large number of organic compounds suggested a similar reaction with cellulose to provide a chemically modified cellulose.

The polymerization of ethyleneimine itself on cotton fabric was studied by Church<sup>7</sup> and not considered satisfactory as a flame-retardant treatment. However, the combination of the flame-retardant property of phosphorus with the reactivity of the ethyleneimine grouping within a compound appeared feasible as a possible durable flame-resistant treatment.

A simple prototype of such a compound is N, N', N'', -triethylenephosphoric triamide (II), the preparation of which has been reported previously<sup>8</sup>.





The triamide was prepared. The crude product was obtained in high yield and applied to cotton khaki fabric under different conditions. Fabric treated with an acetone solution of the crude triamide and cured for 15 minutes at 110° C. (20.7% add-on) had a soft hand but was not flame resistant after one laundering. With the use of an acetone-water padding solution containing the crude triamide and melamine-formaldehyde resin and subsequent curing for four minutes at 180°C., the treated fabric (13% add-on) passed the Vertical Flame Test after five launderings (87% retention). The sample burned when a lighted match was applied.

TABLE VI

Results of Vertical Flame Tests on Cotton Khaki Fabric Treated with N, N', N''- Triethylenephosphoric Triamide

| Treatment               | Add-on<br>(%)     | 1 Laundering              |                           |                          |                 |              |              |                 | 5 Launderings   |              |              |             |
|-------------------------|-------------------|---------------------------|---------------------------|--------------------------|-----------------|--------------|--------------|-----------------|-----------------|--------------|--------------|-------------|
|                         |                   | AF <sup>a</sup><br>(sec.) | AG <sup>b</sup><br>(sec.) | CL <sup>c</sup><br>(in.) | Ret.<br>(%)     | AF<br>(sec.) | AG<br>(sec.) | CL<br>(in.)     | Ret.<br>(%)     | AF<br>(sec.) | AG<br>(sec.) | CL<br>(in.) |
| Triamide                | 20.7              | 0                         | 0                         | 4                        | 26 <sup>e</sup> | 30           | 0            | BC <sup>d</sup> |                 |              |              |             |
| Triamide +<br>M-F Resin | 6.7 <sup>e</sup>  | 28                        | 0                         | BC                       |                 |              |              |                 |                 |              |              |             |
| Triamide +<br>M-F Resin | 13.1 <sup>f</sup> | 0                         | 0                         | 3                        | 92              | 0            | 0            | 3.5             | 87 <sup>e</sup> | 0            | 0            | 3.4         |

<sup>a</sup> AF - Afterflame.

<sup>b</sup> AG - Afterglow.

<sup>c</sup> CL - Char Length.

<sup>d</sup> BC - Burned completely.

<sup>e</sup> These samples burned when an ignited match was applied.

<sup>f</sup> Three seconds AF when an ignited match was applied.

<sup>g</sup> Seven seconds AF when an ignited match was applied.

Further study of the triamide in its application as a flame retardant for cotton fabric is in progress.

### Experimental

Polymerization of Triallyl Phosphate in Chloroform.- A mixture of 740 g. of undistilled triallyl phosphate and 740 g. of chloroform was heated to reflux in a three-necked 2 l. round-bottomed flask, fitted with a stirrer, thermometer, 5 ml. pipette and reflux condenser. Benzoyl peroxide (14g.) was added to initiate the reaction. The mixture was heated at reflux. The reaction was followed by temperature change and the time of efflux of a 5 ml. sample of the reaction mixture (relative viscosity) from the pipette. A threefold increase in viscosity was observed after 150 minutes. The flask was then cooled in cold water to stop the reaction. The mixture was poured into excess petroleum ether; the precipitated polymeric products were washed a few additional times with petroleum ether to remove low molecular weight products and monomer. The resulting product was powdered in a Waring Blendor in the presence of wash solvent and isolated by suction filtration to yield 257 g. (35% conversion) of a white amorphous polymer.

Polymerization of Triallyl Phosphate in Chloroform (Semi-pilot Plant Scale.- A mixture of 10 l. (11kg.) of undistilled triallyl phosphate and 7.3 l. (11kg.) of chloroform was heated to reflux in a three-necked 45 l. round-bottomed flask, fitted with stirrer, thermometer, 5 ml. pipette and reflux condenser. Benzoyl peroxide (215 g.) was added cautiously. The mixture was heated at reflux until the viscosity had increased to three times that observed for the mixture immediately after addition of the peroxide (170 min.). The reflux temperature decreased from 86° C., observed initially, to 81.7° C.

The polymeric product from a sample of the reaction mixture was precipitated by the addition of petroleum ether. The resulting powdered product was obtained in 35 per cent conversion.

The petroleum ether was removed from the washings by distillation at reduced pressure ( $65^{\circ}\text{C.}$ , 14 mm.). The residue was transferred to a polymerization apparatus and heated. Chloroform (2.8 kg.) was added slowly until the reflux temperature of the mixture was  $85^{\circ}\text{C.}$  Benzoyl peroxide (20 g.) was added. The polymerization required 120 minutes. The conversion was 34-36 per cent.

Polymerization of Triallyl Phosphate in Halomethanes.— The benzoyl peroxide induced solution polymerization of triallyl phosphate in carbon tetrachloride, bromochloromethane, bromodichloromethane, bromotrichloromethane, bromoform and mixtures of some of the above with chloroform were completed in the manner described for the reaction in chloroform.

Diallyl  $\alpha$ -Carbethoxyethyl Phosphate. — Into a three-necked 2 l. round-bottomed flask, equipped with stirrer, dropping funnel and reflux condenser were placed 138 g. (0.9 mole) of phosphorus oxychloride and 200 ml. of dry toluene. The solution was cooled to  $-30^{\circ}\text{C.}$ , and a solution of ethyl lactate (108 g., 0.91 mole), pyridine (73 g., 0.92 mole), and toluene (200 g.) was added dropwise with stirring. The reaction mixture was stirred for 15 minutes and a solution of allyl alcohol (117 g., 2 moles), pyridine (160 g., 2 moles) and toluene (200 ml.) was added dropwise with stirring. Water was then added to dissolve the precipitated pyridine hydrochloride. The toluene layer was washed successively with water and 5 per cent aqueous sodium carbonate solution and then dried over anhydrous sodium carbonate. The toluene was removed by distillation under reduced pressure to yield 163 g. (65%) of the clear crude ester, which could not be distilled.

Diallyl  $\beta$ -Bromopethyl Phosphate.- A mixture of 183 g. (1.25 moles) of phosphorus oxychloride and 300 g. of toluene was placed in a three-necked 2 l. round-bottomed flask, fitted with stirrer, dropping funnel and reflux condenser, and cooled to  $-30^{\circ}$  C. A solution of 150 g. (1.25 moles) of ethylene bromohydrin, 96 g. (1.21 moles) of pyridine and 100 g. of toluene was then added dropwise with stirring. The mixture was stirred for 15 minutes and a solution of 180 g. (3.1 moles) of allyl alcohol, 192 g. (2.4 moles) of pyridine and 150 g. of toluene was then added dropwise with stirring. After the addition was completed, water was added to dissolve the precipitated pyridine hydrochloride. The toluene layer was washed with water and 5% aqueous sodium carbonate solution and dried over anhydrous sodium carbonate. The toluene was removed by distillation under reduced pressure to yield 277 g. (82%) of the crude ester.

Reaction of Ethylene Diamine with Phosphorus Oxychloride.- To a solution of 50 g. of phosphorus oxychloride in 200 ml. of chloroform contained in a three-necked 1 liter round-bottomed flask, equipped with stirrer, dropping funnel and reflux condenser, was added a solution of 50 g. of ethylene diamine in 50 ml. of chloroform in a dropwise manner at room temperature over a period of 30 minutes. The reaction was exothermic and was controlled by cooling the flask in water. The stirring was continued for an additional 30 minutes at room temperature. Initially the polymeric product separated as a viscous liquid. At the end of the stirring period it had become an amorphous-like near solid. The yield of product was 70 g.

Reaction of Diethylene Triamine with Phosphorus Oxychloride. - A solution of 100 g. of diethylene triamine in 450 g. of chloroform contained in a three-necked 2 liter Morton flask, equipped with high speed Morton stirrer, dropping funnel and reflux condenser, was heated to reflux.

Phosphorus oxychloride (61 g.) was added slowly with moderate stirring. The heat was removed from the flask as the reaction became violent. A near white viscous material precipitated from the reaction mixture when the oxychloride was added.

The reaction mixture together with an additional 14 g. of phosphorus oxychloride was transferred to a Waring Blendor and the polymeric product powdered. During this process aqueous concentrated hydrochloric acid solution was added to reduce the pH to 4-6. The resulting amorphous solid was separated by suction filtration, washed twice with chloroform and dried in a desiccator under reduced pressure. The yield of near white powder was 154 g.

N, N', N''-Triethylenephosphoric Triamide. - The triamide was obtained in 51-99% crude yield as an oil according to the procedure of Bestian,<sup>8</sup> who reported the pure product a low melting solid. Experiments to purify the crude oil by vacuum distillation resulted in rapid decomposition and explosion.

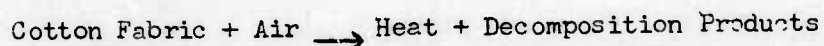
To 150 g. of a 23% solution of the crude triamide in acetone were added 150 g. of a 20% aqueous solution of Aerotex Resin UM special and 9 g. of Aerotex Accelerator UTX solution. A sample of cotton khaki fabric was treated with this solution (66% pickup), dried at 80° C. for 15-20 min. and cured at 180° C. for 4 min. The treated fabric was rinsed in cold water for 15 min. and dried at 80° C. The per cent add-on was 13.4.

The Thermal Decomposition of Cellulose

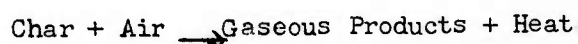
The study of the effects of various treatments on the thermal degradation of cellulose has been extensive <sup>7, 9</sup>. Much of the work was completed in order to learn more concerning the mechanism of the thermal decomposition of cellulose since such knowledge would be beneficial in the design of fire resistant treatments for cellulosic fabrics. However, the mechanism has remained unclear partly because of insufficient fundamental data.

At elevated temperatures cellulose decomposes to produce three main fractions, a carbonaceous residue (char), a flammable tar distillate and a volatile fraction containing water and gases.<sup>10</sup> The properties of these products has been studied by a number of investigators and the results have been summarized by Hurd<sup>11</sup> and Heuser<sup>12</sup>. Marked changes in the ratio of the three types of decomposition products have been observed by Church<sup>13</sup> and Coppick<sup>14</sup> upon treatment of cellulose with various reagents. With the application of fire retardants an increased formation of the char and volatile fractions and a decreased amount of tar distillate were observed. Increase of the water and gas volatile fraction was not considered important since the same effect was observed by treatment of cellulose with inert substances. The change in char and tar fractions, however, appeared to be influenced by application of fire retardants. Several investigations have been based on the ability of various treatments to effect these changes.

While studies on the over-all changes have been important in attempts to develop a plausible mechanism for the thermal decomposition of cellulose, equally important have been the studies on the decomposition reaction rates. Most of the investigations were completed by Church<sup>15</sup> and Coppick<sup>16</sup> and included the study of both pyrolysis and combustion reactions. The results indicated that in an oxidizing atmosphere cotton fabrics decompose in two exothermic stages<sup>17</sup>, with the first associated with the breakdown to and some oxidation of the tar products.



The second step was associated with the oxidation of the charred residue.



Cotton fabrics heated in an inert atmosphere (pyrolysis) were observed to decompose in a single stage to give char, tar and gaseous products without heat evolution.

A substantial part of the Quartermaster Corps sponsored research conducted at the University of Rhode Island has been devoted to a study of the thermal decomposition of cellulose (cotton fabric) under pyrolytic conditions. Rates of decomposition at different temperatures for untreated and variously treated fabric samples were investigated. Based upon this kinetic data and the observations reported in the literature by other investigators, a mechanism for the pyrolysis has been proposed.

In addition, a study of the insulation to heat provided by some treatments on cotton fabric and that provided by different cotton-wool blends has been completed.

#### Mechanism of the Pyrolytic Decomposition of Cellulose

The pyrolysis of cotton fabric treated with different compounds was completed at various temperatures in a study of the effect of the treatments on the quantity of char formed. The following table summarizes the results and illustrates the increase in char formation with treatment.

TABLE VII

Effect of Various Compounds on Char Formation  
in the Pyrolysis of Cotton Khaki Fabric

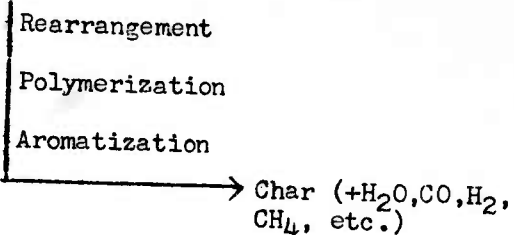
| <u>Temp. (°C.)</u>  | <u>Per Cent of Char Formed at:</u> |            |            |            |            |
|---|------------------------------------|------------|------------|------------|------------|
|   | <u>200</u>                         | <u>250</u> | <u>300</u> | <u>400</u> | <u>500</u> |
| <u>Sample</u>   |                                    |            |            |            |            |
| Untreated fabric  |                                    | 93.3       | 43.2       | 16.6       | 11.4       |
| Fabric treated with:  |                                    |            |            |            |            |
| NH <sub>4</sub> Cl (10%)  | 68.4                               |            | 51.4       | 38.4       | 30.8       |
| NH <sub>4</sub> Br (10%)  | 59.6                               |            | 50.9       | 39.8       | 33.3       |
| Na <sub>2</sub> B <sub>4</sub> O <sub>7</sub> • 10 H <sub>2</sub> O (10.2%) | 95.6                               |            | 50.4       | 37.6       | 30.7       |
| NaH <sub>2</sub> PO <sub>4</sub> • H <sub>2</sub> O (11.2%)                 | 93.0                               |            | 52.6       | 40.8       | 34.0       |
| NH <sub>4</sub> H <sub>2</sub> PO <sub>4</sub> (10.1%)                      | 61.4                               |            | 50.0       | 42.0       | 35.7       |
| (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> (9.2%)                     | 61.8                               |            | 49.4       | 42.5       | 35.6       |
| NaHCO <sub>3</sub> (7%)   | 83.3                               |            | 36.9       | 27.5       | 23.6       |
| Na <sub>2</sub> C <sub>2</sub> O <sub>4</sub> (6.6%)                        | 94.4                               |            | 38.6       | 24.9       | 20.2       |
| CuBr <sub>2</sub> (7.7%)  | 59.8                               |            | 47.1       | 36.6       | 29.2       |
| TAP-CHCl <sub>3</sub> polymer (14%)   | 64.6                               |            | 48.1       | 38.7       | 31.1       |
| Br poly TAP (19%)   | 67.5                               | 54.1       | 47.0       | 36.4       | 29.2       |
| Br poly TAP (10%)   | 80.4                               |            | 45.5       | 34.9       | 28.8       |
| Br TAP (10.9%)  | 70.6                               |            | 42.2       | 33.5       | 28.2       |
| TAP-CH Br <sub>3</sub> emulsion<br>polymer (7.8%)                           | 62.1                               |            | 39.8       | 29.6       | 25.3       |
| Diallyl Melamine (6.7%)   | 96.1                               |            | 44.8       | 25.2       | 17.0       |
| Br diallyl Melamine<br>(6.8%)   | 61.2                               |            | 43.8       | 33.4       | 26.2       |
| T H P C (16%)   | 94.9                               |            | 50.8       | 38.6       | 33.3       |
| Erifon (16.3%)  | 98.5                               |            | 47.9       | 40.2       | 35.6       |



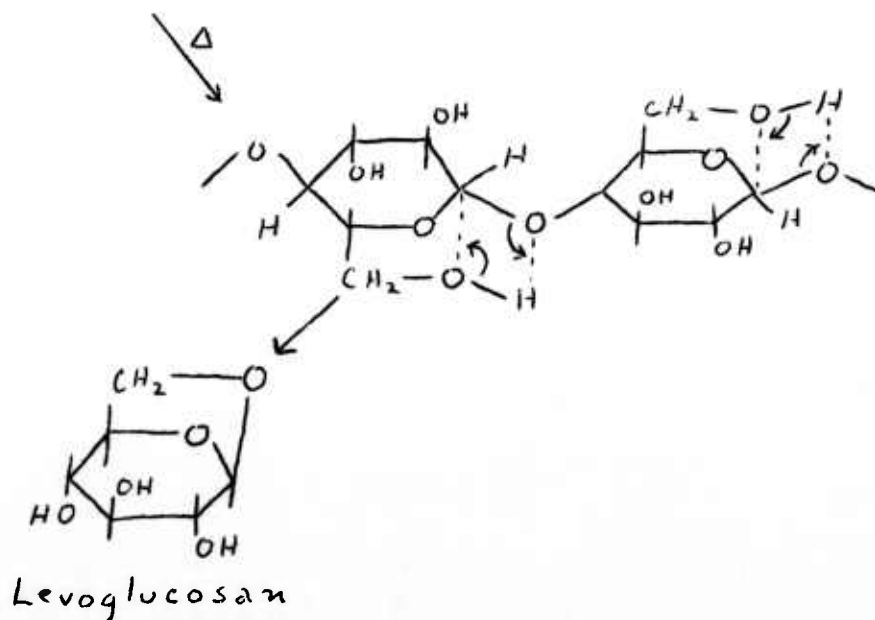
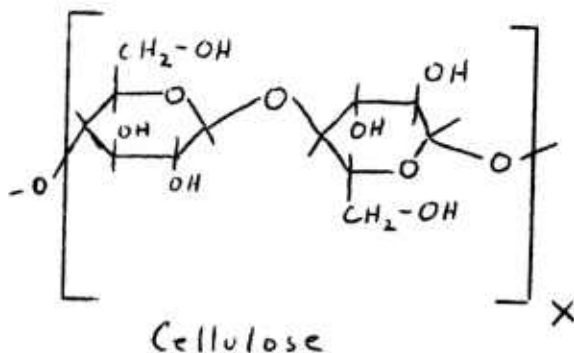
The observation that the rates of thermal decomposition of linen fabric, cotton fabric, rayon fabric, hydrocellulose and glucose increased in the order stated (Figure 4 ) suggested a common mechanism for the pyrolysis of cellulosic materials regardless of degree of polymerization. Additional evidence for this postulate was provided by the constancy in resulting pyrolysis chars (Figure 5 ).

The rates of pyrolysis of untreated and treated cellulose samples were investigated and found to follow first-order kinetics (Figure 6 ). The rates were not affected by diphenylamine or hydroquinone, indicating that a free radical process was not involved in the rate-determining process. Relative rates of reaction and energies and entropies of activation were obtained and are given in Table VIII. The activation energies were obtained in the usual manner by plotting logarithm of rate constant against reciprocal of the absolute temperature. From the series of parallel lines obtained in Figure 7 it can be seen that the samples studied possessed a fairly constant energy of activation ( $33 \pm 3$  kcal.).

The results suggested a common intermediate for the pyrolysis of untreated and treated cellulosic samples and were consistent with the mechanism outlined by Tamaru<sup>18</sup> which proposed that the pyrolysis of cellulose first involved a depolymerization followed by the competing reactions of destructive distillation and char formation. The isolation of a glucose anhydride, 1, 6-anhydro- $\beta$ -D-glucopyranose (levoglucosan or  $\beta$ -glucosan), in 30-40 per cent yield from the destructive distillation of cellulose by Pictet and Sarasin<sup>19</sup> supported the belief that a common intermediate was involved.



The formation of levogluconan could result from an intramolecular displacement.



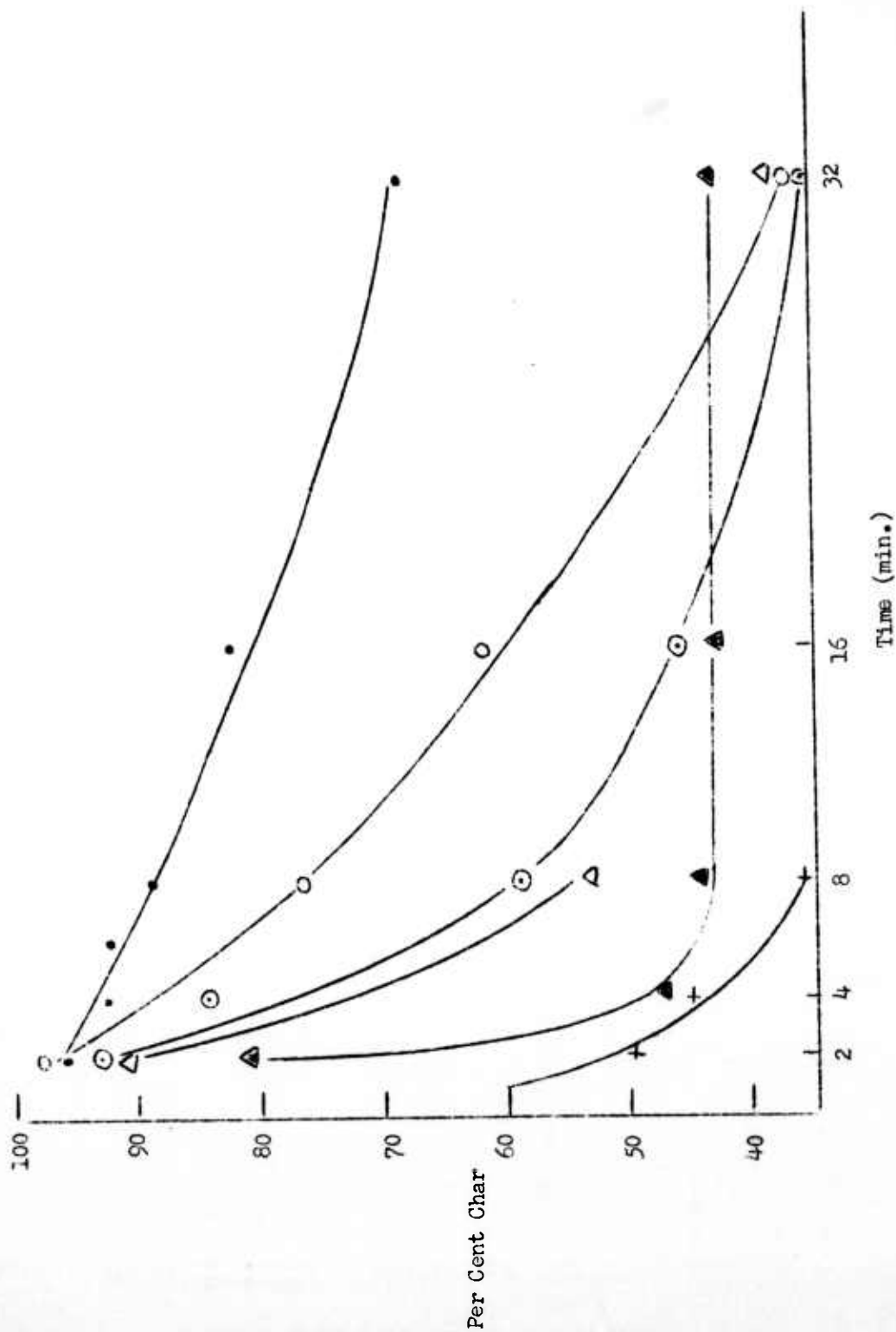


Figure 4. Rate of thermal decomposition at 325° C. of linen, ●; cotton, ○; rayon, ⊙; hydrocellulose, Δ; cotton treated with 10% Br poly TAP, ▲; glucose, +.

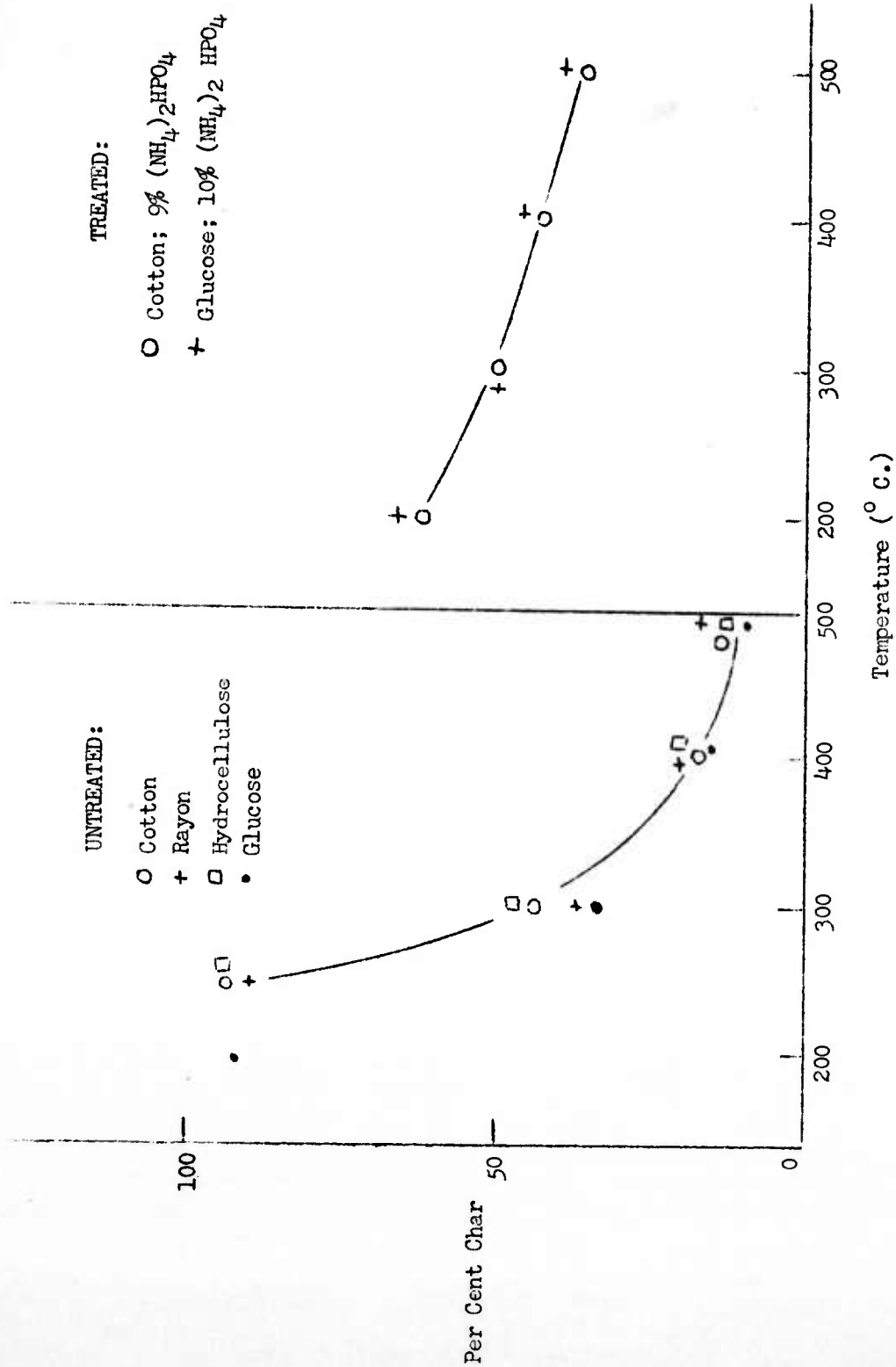


Figure 5. Pyrolysis of untreated and treated cellulosic samples of varying degrees of polymerization at different temperatures.

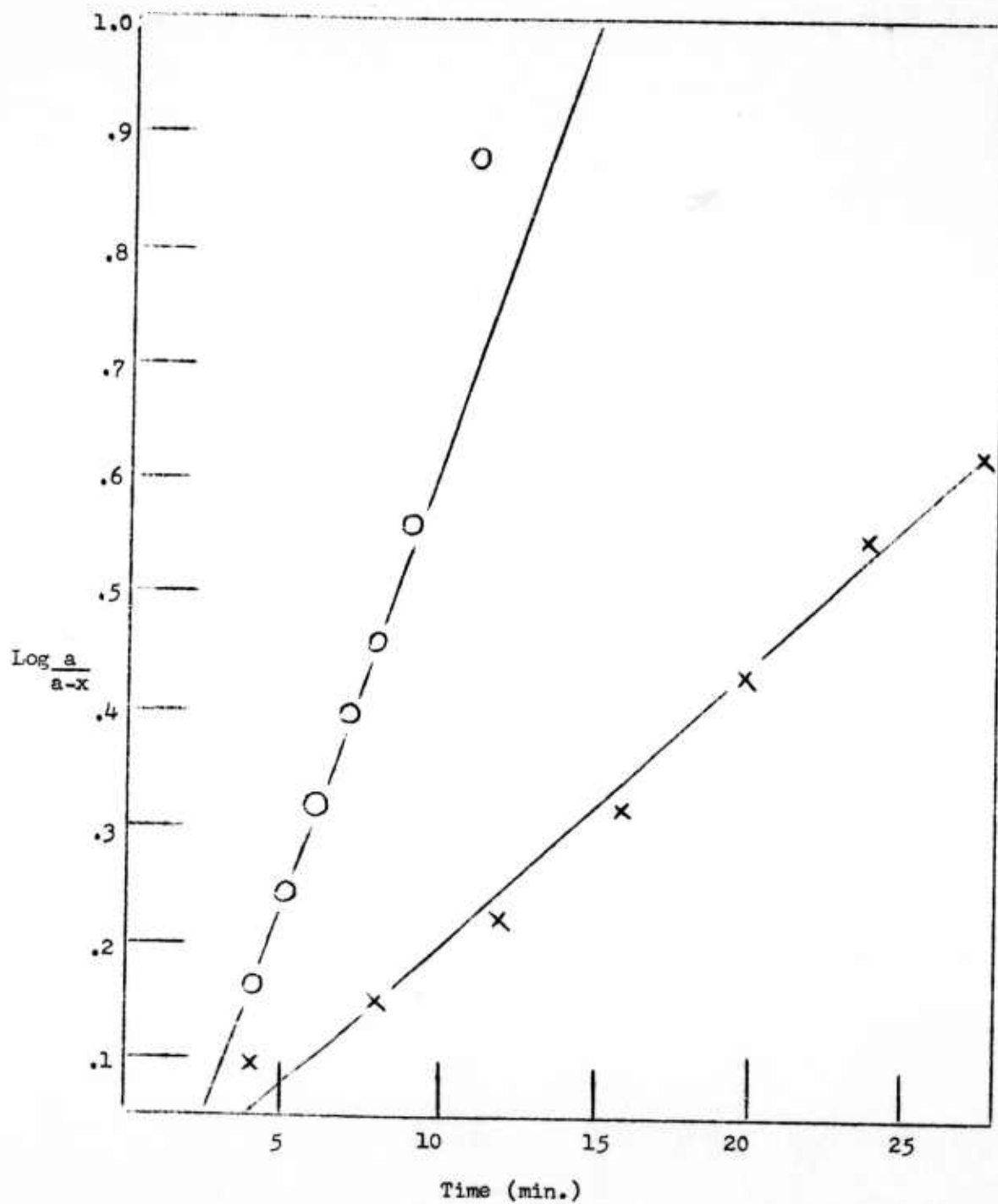


Figure 6. First-order curves for the pyrolysis of absorbent cotton at 300° C., x; and 325° C., O.

TABLE VIII  
Relative Rates and Entropies of Activation for the Pyrolysis of  
Treated and Untreated Cellulose

| <u>Cellulose Sample</u> | <u>Rel. Rate at 300° C.</u> | <u><math>\Delta S^*</math> at 300° C. (e.u.)</u> | <u><math>\Delta S^*</math> Relative to Cotton (e.u.)</u> |
|-------------------------|-----------------------------|--|--|
| Cotton                  | 1.0                         | -14.4  | 0.0  |
| Linen                   | 0.7                         | -15.2  | -0.4   |
| Rayon                   | 2.8                         | -12.3  | 2.1  |
| Cotton Treated with:    |                             |  |  |
| 0.8% $KClO_4$           | 1.5                         | -13.5  | 0.9  |
| 1.6% $NaCl$             | 1.7                         | -13.3  | 1.1  |
| 1.5% $Na_2CO_3$         | 1.9                         | -13.1  | 1.3  |
| 1.7% $LiCl$             | 14.5                        | - 9.1  | 4.3  |
| 0.8% $(NH_4)_2 HPO_4$   | 4.2                         | -11.5  | 2.0  |
| 1.7% $(NH_4)_2 HPO_4$   | 17.5                        | - 8.7  | 5.7  |

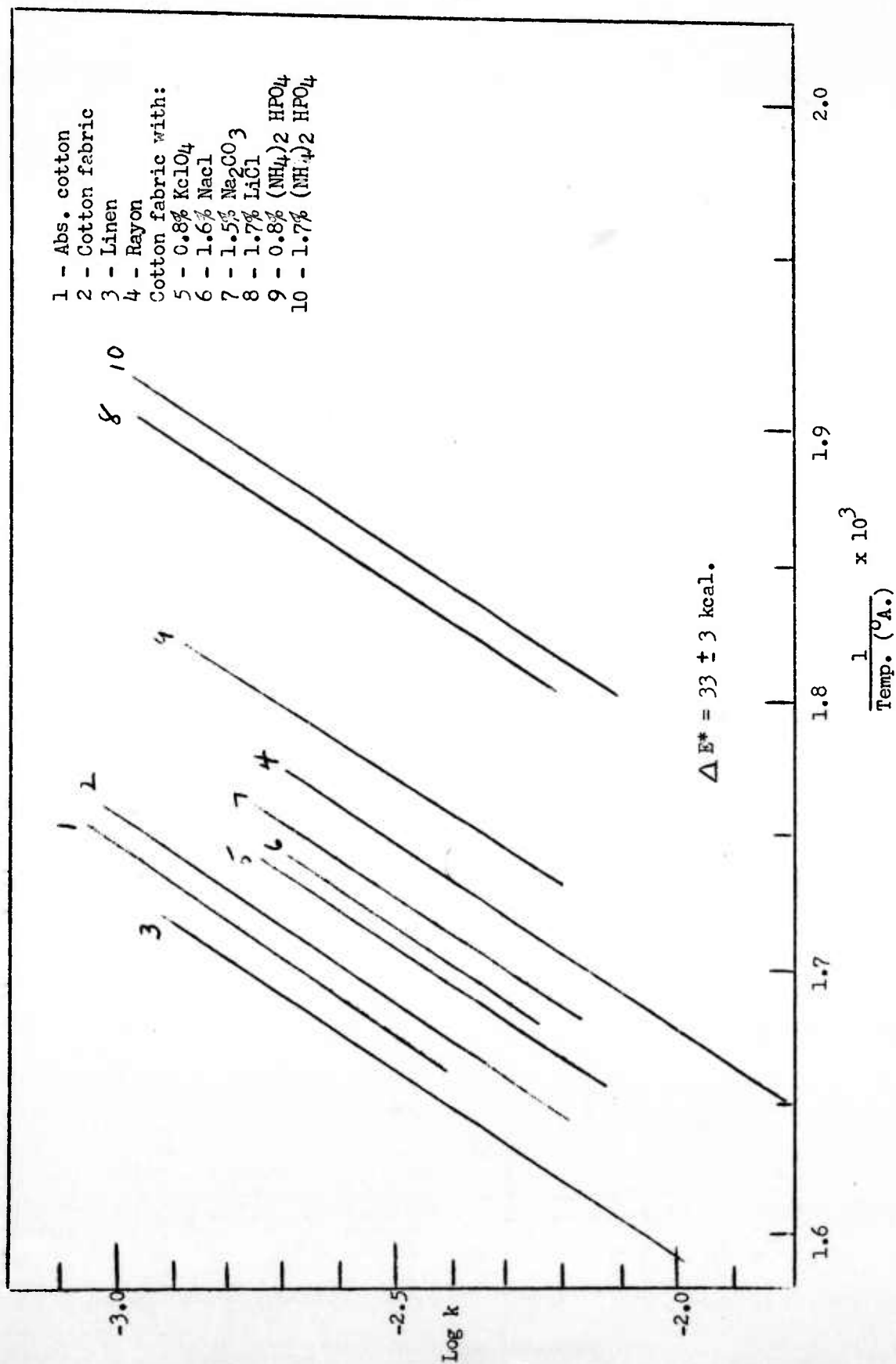


Figure 7. Determination of activation energy for the pyrolysis of untreated and treated cellulose.

The results of experiments changing the heating rate of the pyrolysis indicated that the destructive distillation process (tar formation was favored by increased rates of applied thermal energy (Table IX).

TABLE IX

Effect of Heating Rate on the Decomposition Products (Char/Tar Ratio) from the Pyrolysis of Cotton Khaki Fabric.

| Sample  | 400° C.                       |                               | 500° C.                       |                               |
|---|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
|   | Slow <sup>a</sup><br>Char/Tar | Fast <sup>b</sup><br>Char/Tar | Slow <sup>a</sup><br>Char/Tar | Fast <sup>b</sup><br>Char/Tar |
| Untreated fabric                                      | 0.45                          | 0.36                          | 0.49                          | 0.23                          |
| Fabric treated with:                                  |                               |                               |                               |                               |
| 9.2% (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> | 3.93                          | 2.57                          | 2.96                          | 2.24                          |
| 16% T H P C   | 3.90                          | 2.54                          | 3.50                          | 2.12                          |
| 19.2% Br poly TAP                                     | 2.09                          | 1.58                          | 1.88                          | 1.18                          |

<sup>a</sup> The samples were placed in test tubes in an electrically heated aluminum furnace block at room temperature. The block was heated to the desired temperature and the pyrolysis continued for 60 minutes. A period of 30 minutes was required for the block to be heated to the desired temperature.

<sup>b</sup> The furnace was preheated to the desired temperature before the samples were introduced. The pyrolysis was continued for 60 minutes.

The observed constancy in the energy of activation indicated that the low add-on of the fire retardants studied did not have a catalytic effect on the decomposition. The increased activation entropy observed indicated that the low add-on of treatments studied decreased the cohesion of the cellulose chains and hence increased the rate of thermal decomposition.



The data for the kinetic studies described were obtained under conditions in which the temperature variation during individual rate determinations was  $5-10^{\circ}\text{C}$ . Since such experiments require very precise temperature control, the control unit for the investigation was modified by incorporating a capacitance switch to obtain a temperature variation of  $\pm 0.5^{\circ}\text{C}$ . With the modified apparatus further kinetic studies have been started. The program includes the repeating of the previous work for re-evaluation and the study of increasing add-on of various treatments on the decomposition of cotton fabric.

In recent experiments the rates of pyrolytic decomposition of untreated linen and cotton khaki fabric, untreated and treated with melamine-formaldehyde resin, melamine, formaldehyde and brominated triallyl phosphate polymer were studied. In Figures 8-14 the first-order curves obtained are given. Table X summarizes the activation energies ( $300^{\circ}\text{C}$ .) obtained. With the use of an efficient temperature control apparatus an activation energy for the pyrolysis of untreated fabric approximately 10 kcal. greater than that observed previously in this laboratory was obtained. A relatively constant energy of activation ( $43 \pm 4$  kcal.) was observed for the majority of the samples studied; however, the value obtained for the fabric treated with brominated triallyl phosphate polymer (7% add-on) was approximately 10 kcal. less than that observed for the untreated fabric. The study of the effect of increasing add-on of treatment should provide a possible explanation of this difference.

The results obtained for the pyrolysis of untreated linen are in apparent disagreement with those of the earlier studies. Flax fibers from which linen is spun, possess a more highly ordered arrangement of the constituent cellulose chains than cotton fibers, as revealed by microscopic study<sup>20</sup>. The more highly ordered state in linen would be expected to be characterized by a thermal stability greater than that for cotton.

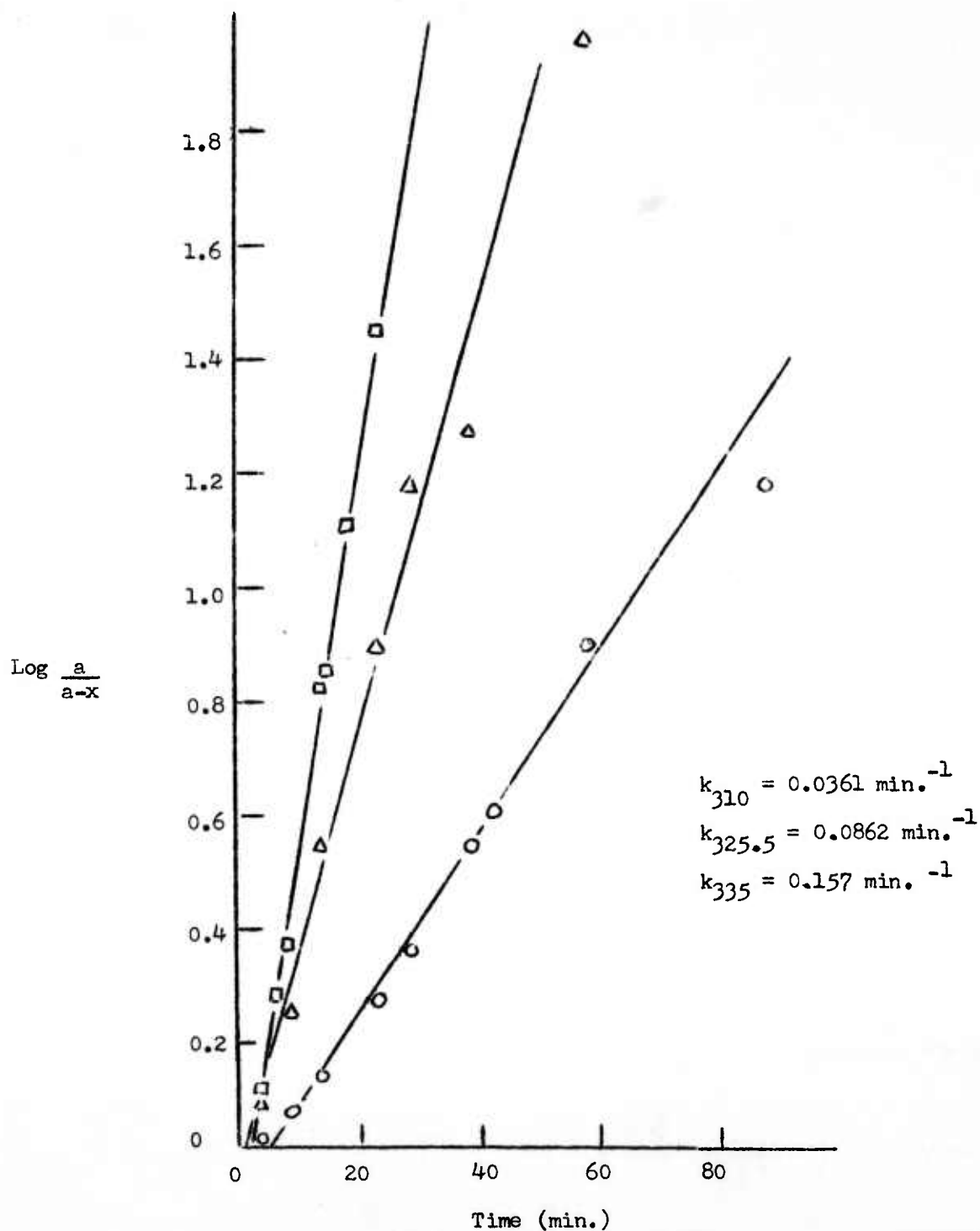


Figure 8. First-order curves for the pyrolysis of untreated linen at 310° C., ○; 325.5° C., △; 335° C., □.

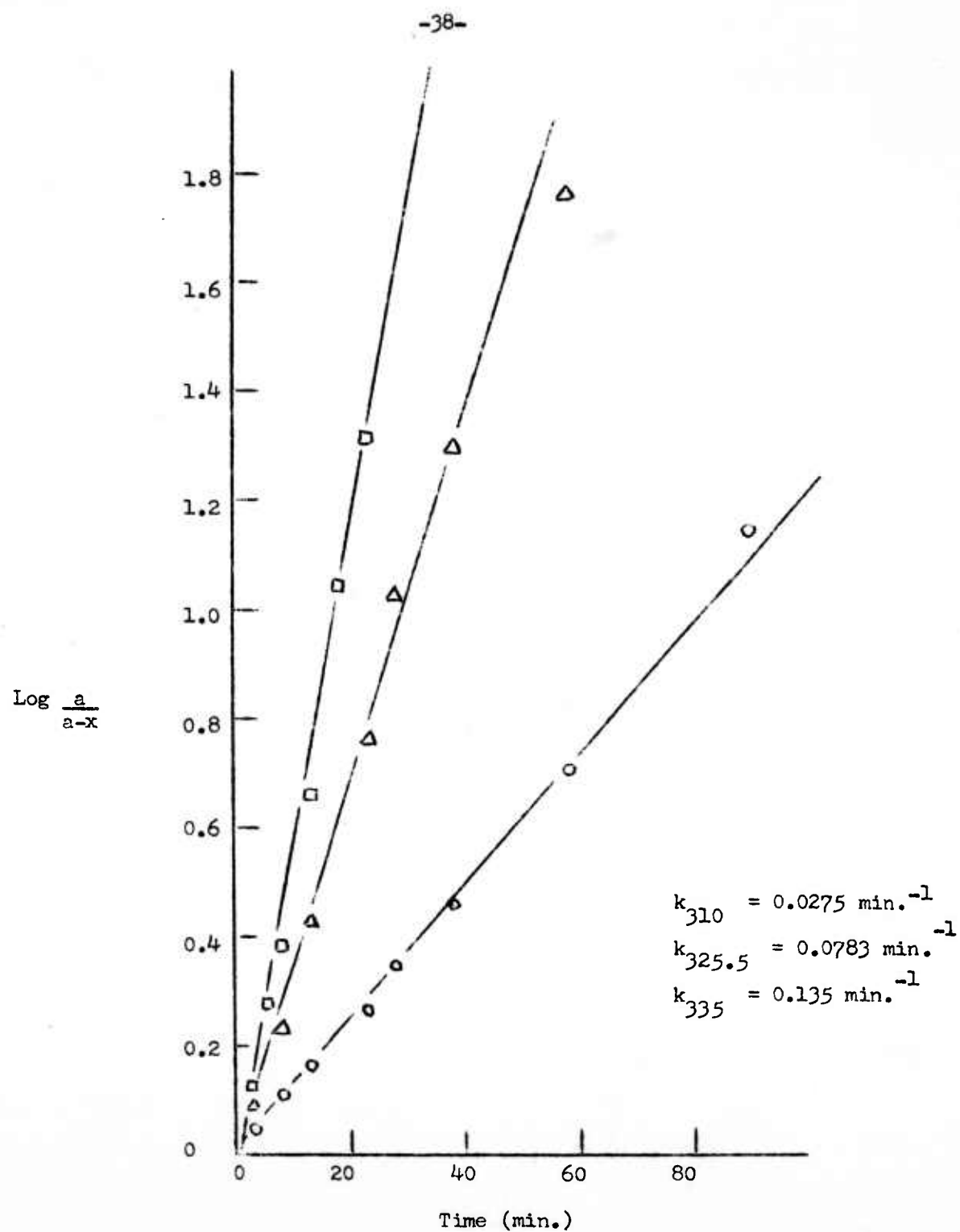


Figure 9. First-order curves for the pyrolysis of untreated cotton at 310° C., ○; 325.5° C., △; and 335° C., □.

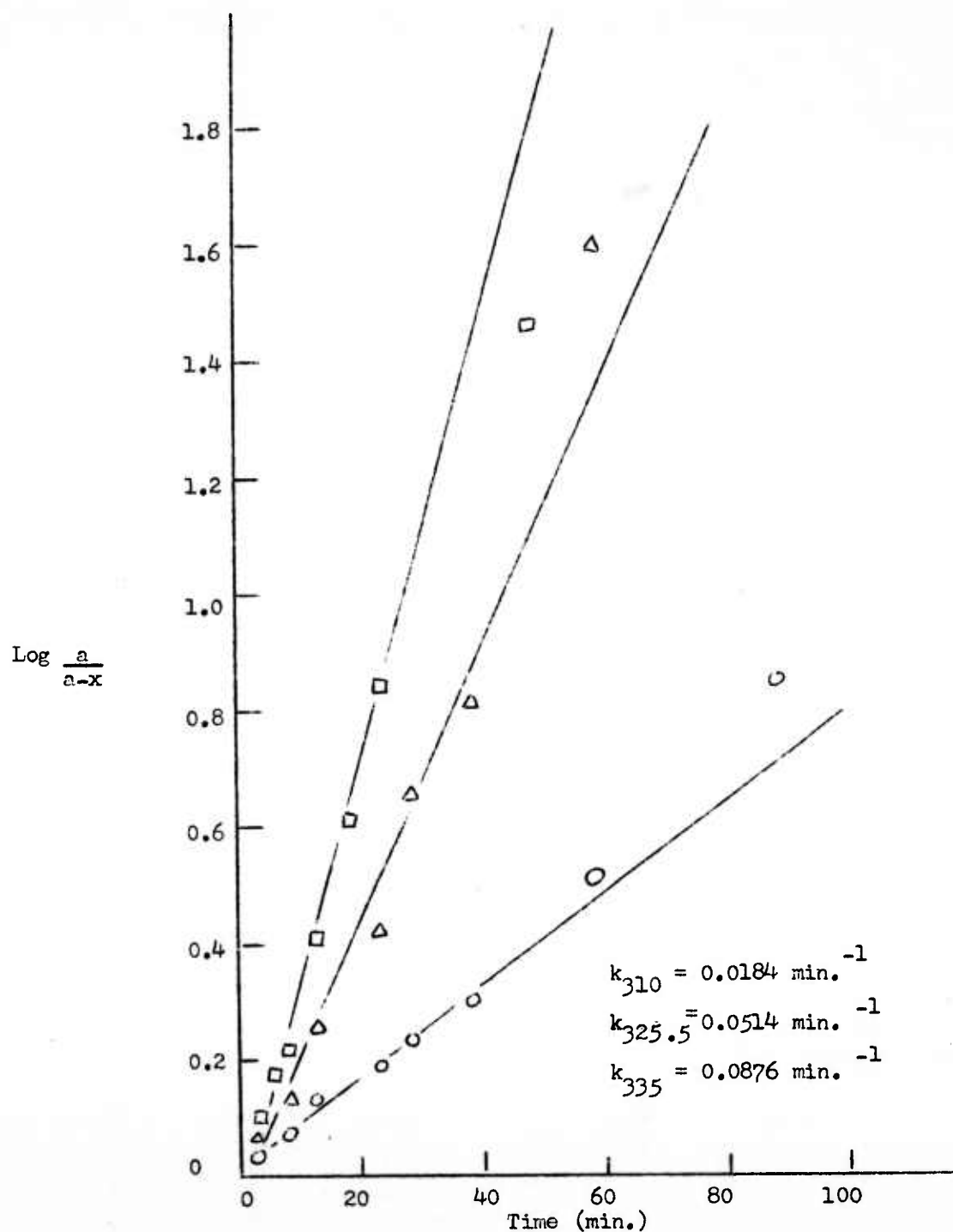


Figure 10. First-order curves for the pyrolysis of cotton khaki fabric treated with 3% melamine-formaldehyde resin at 310° C., O; 325.5° C., Δ; and 335° C., □.

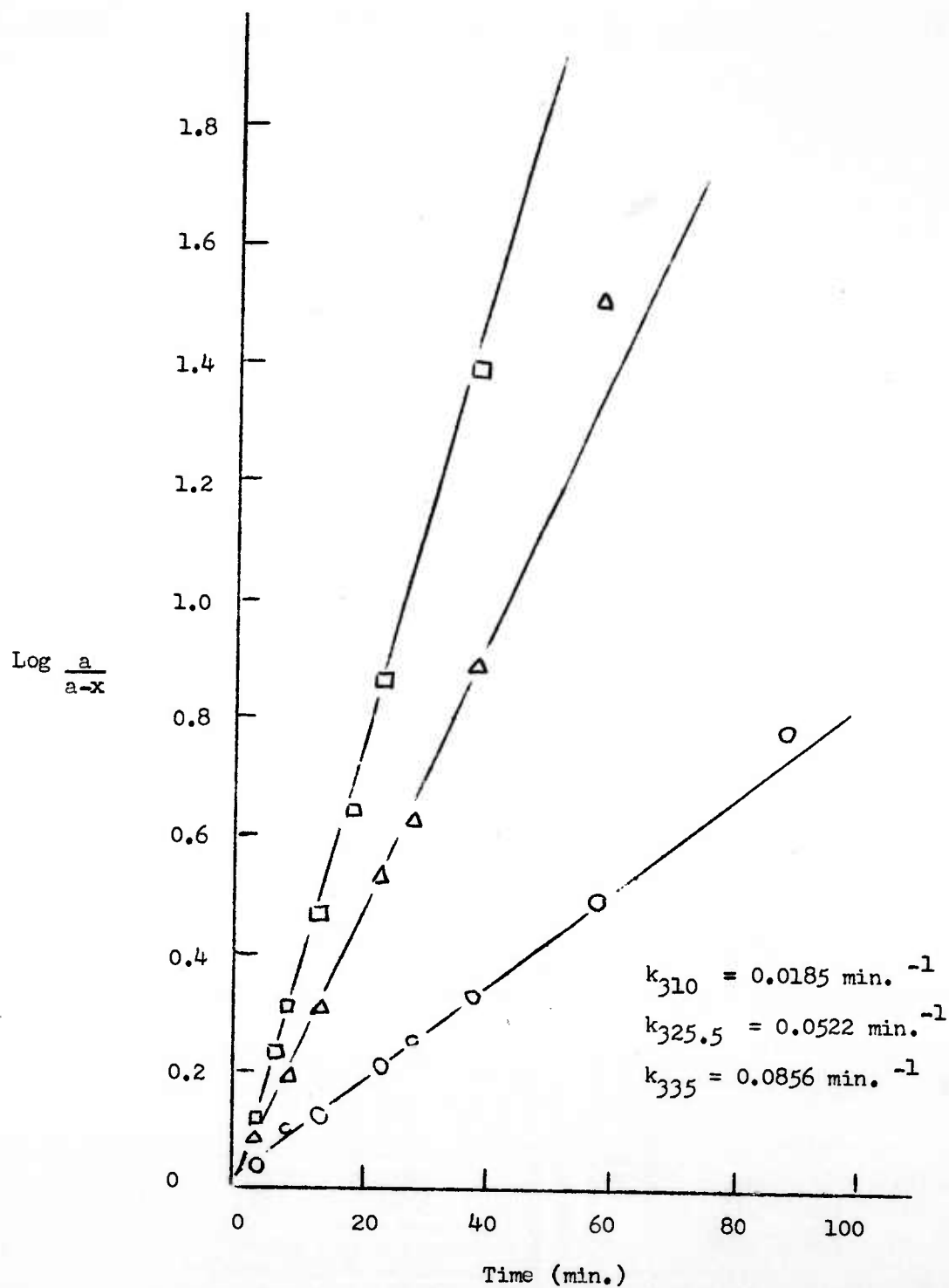


Figure 11. First-order curves for the pyrolysis of cotton khaki fabric treated with 7.4% melamine-formaldehyde resin at 310° C., ○; 325.5° C., Δ; and 335° C., □.

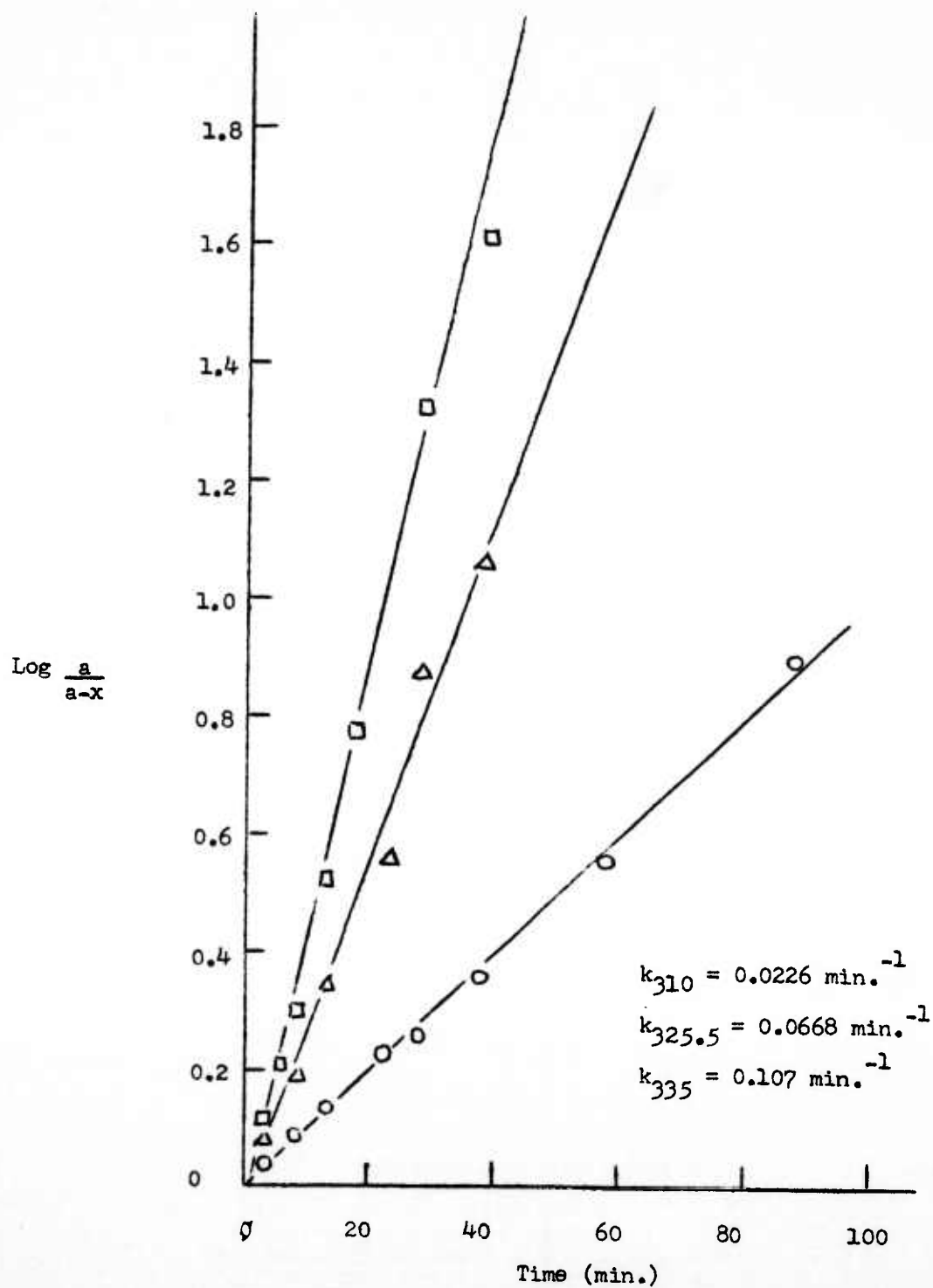


Figure 12. First-order curves for the pyrolysis of cotton khaki fabric treated with 1.5% melamine at 310° C., O; 325.5° C., Δ; and 335° C., □.

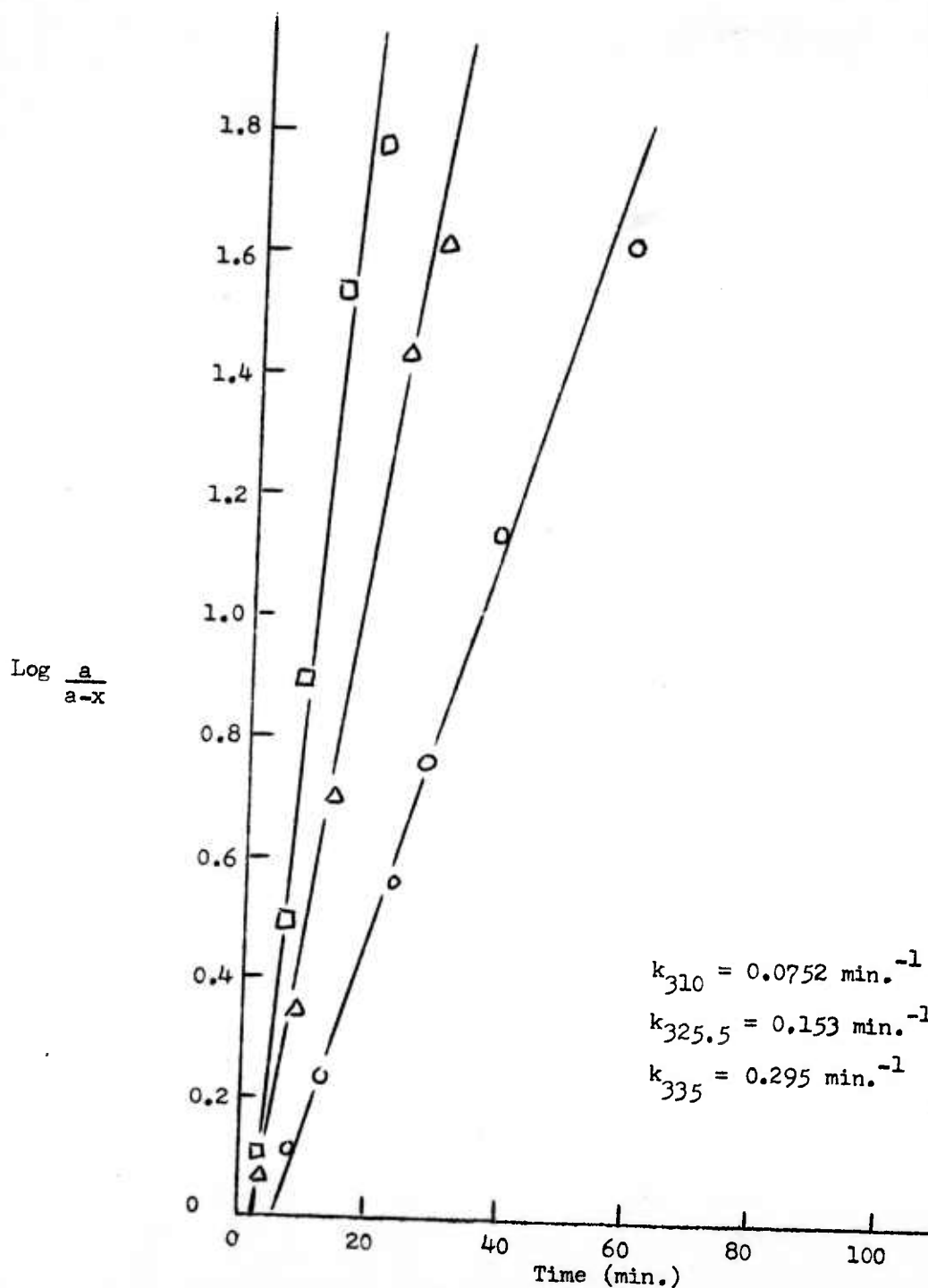


Figure 13. First-order curves for the pyrolysis of cotton khaki fabric treated with 0.6% fixed formaldehyde at 310° C., ○; 325.5° C., △; and 335° C., □.

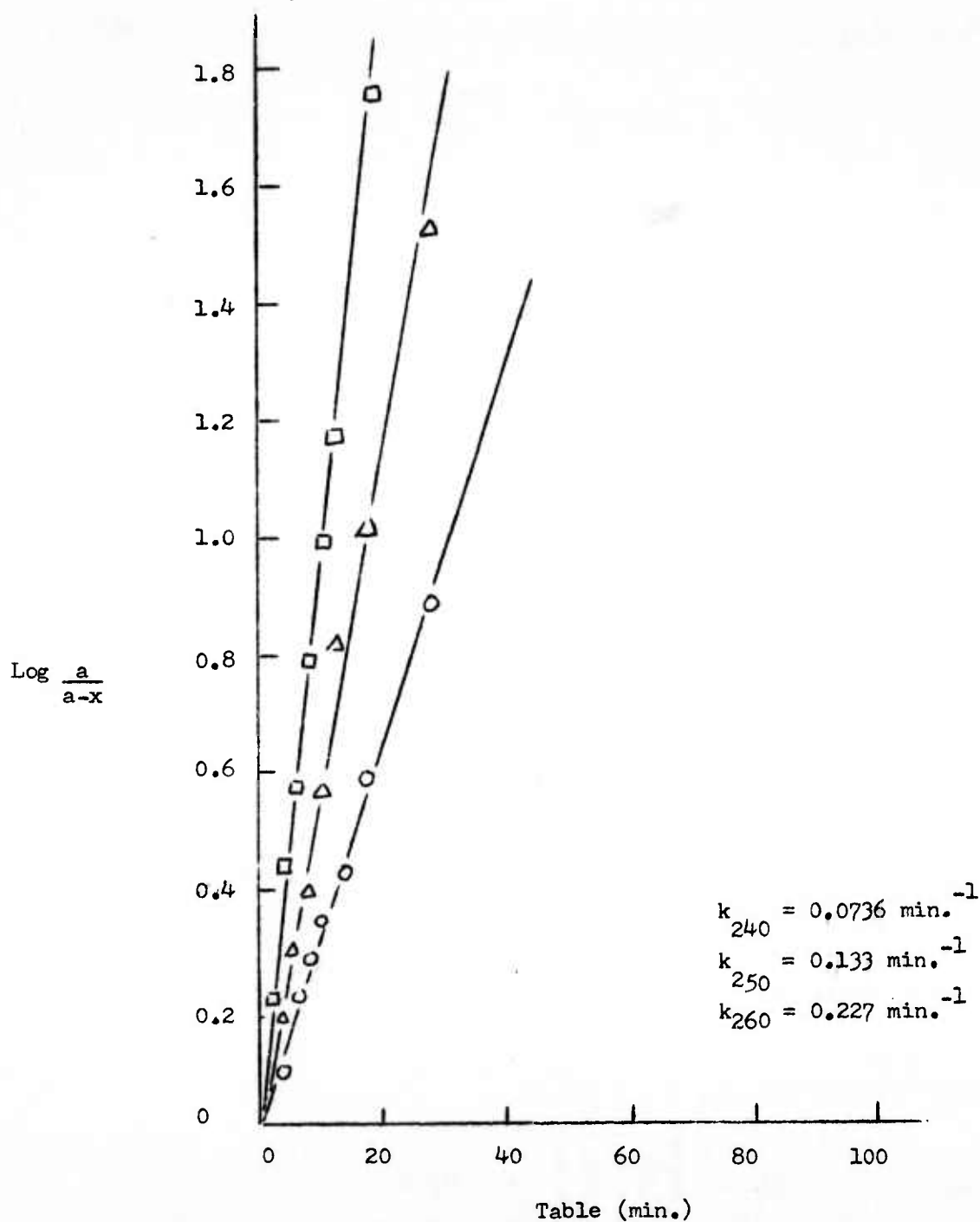


Figure 14. First-order curves for the pyrolysis of cotton khaki fabric treated with 7% brominated triallyl phosphate polymer at 240° C., O; 250° C., Δ; and 260° C., □.



T A B L E X

Relative Rates and Activation Energies for the Pyrolysis of  
Untreated and Treated Cellulosic Samples at 300° C.

| Sample  | Specific Rate Constant<br>(min. <sup>-1</sup> ) | Relative Rate | Activation Energy<br>(kcal.) |
|---|---|---------------|------------------------------|
| Untreated linen fabric                        | 0.0190  | 1.32          | 41.6                         |
| Untreated cotton khaki fabric                 | 0.0144  | 1.00          | 44.4                         |
| Cotton khaki fabric treated with:             |   |               |                              |
| 3.0% Melamine-formaldehyde resin              | 0.0097  | 0.67          | 43.7                         |
| 7.4% Melamine-formaldehyde resin              | 0.0010  | 0.69          | 43.1                         |
| 1.5% Melamine                                 | 0.0120  | 0.83          | 44.0                         |
| 0.6% Formaldehyde                             | 0.0402  | 2.79          | 39.1                         |
| 7.0% Brominated Triallyl<br>Phosphate Polymer | 2.0300  | 139.00        | 32.2                         |

However, the recent results, summarized in Table X, were anomalous. The rate of pyrolysis for untreated linen was observed to be consistently greater than that for untreated cotton khaki fabric at three different temperatures. Previously linen was observed to decompose at a rate slower than that for the cotton fabric. Although both studies were completed using samples from the same piece of linen fabric, the observed anomaly in rates possibly can be attributed to variations in the preparation, weaving and finishing of the fabric. Also, the difference in results obtained might be within the experimental error of the method.

The difference in preparation, weaving and finishing of linen applies also to all commercially obtained fabrics, thereby questioning the choice of cotton khaki fabric as an efficient standard in such a basic study as kinetics of pyrolysis. In order to eliminate this objection a sample of raw field cotton will be obtained, purified and studied.

The data obtained from the study of melamine-formaldehyde resin and melamine-treated cotton khaki fabric indicated a greater thermal stability compared to untreated fabric as evidenced by the slower pyrolysis rates for the treated fabric.

The formaldehyde treatment was applied to fabric according to the procedure of Wagner and Pacsu<sup>21</sup>, whose studies indicated the formation of methylene bridges between the hydroxyl groups of different glucose residues. Such a treatment would chemically modify the cellulose and change the route of pyrolysis. The observed rate was approximately three times that for untreated fabric.

The belief that levoglucosan is the intermediate in the pyrolysis of cellulose was based mainly on the reported isolation of this compound in substantial yield from the destructive distillation of cellulose<sup>19</sup>. Accordingly, the preparation of this anhydro sugar was undertaken to provide a supply for pyrolysis studies in order to test the hypothesis.

Several procedures <sup>19,22,23</sup>, involving the destructive distillation of carbohydrates, were attempted before a satisfactory method was found. Hydrocellulose was pyrolyzed under reduced pressure in an electric furnace according to the procedure of Venn.<sup>24</sup> A 25 per cent yield of levoglucosan (based on the weight of hydrocellulose) was obtained from the resulting crude viscous distillate. Experiments were completed to determine whether the anhydro sugar behaved similarly to cellulose under pyrolytic conditions. The admixture of 10 per cent of diammonium hydrogen phosphate induced an initially greater rate of decomposition as compared with an untreated sample (Figure 15). In addition, the per cent char resulting at different temperatures was greater for the treated than untreated samples. Figures 16 and 17 indicate that untreated and treated levoglucosan react in a manner similar to that of untreated and treated cellulose, hydrocellulose and glucose under pyrolytic conditions.

#### Insulation Studies.

A study of the insulation afforded cotton khaki fabric by melamine-formaldehyde resin and other treatments was completed. The relative insulation was determined by a hot plate method. The fabric sample was placed on the hot plate and covered with an insulated aluminum dish to which a thermocouple was attached. The increase of temperature with time was recorded for each determination (figure 18). The area under each curve was taken as the relative insulation. The variation of char with temperature for melamine-formaldehyde resin treated fabric is given in Figure 19. Figures 20A and 20B indicate a correlation between the insulation effect and resulting char. The average char per unit area was calculated and found to correlate with the insulation obtained. Table XI outlines the results.

The insulation effect is dependent on the average amount of fabric or char between the heat source and receiver over the period of exposure. Figure 20B indicates that the insulation provided by fire retardant-treated cotton khaki fabric is near but less than that given by the fabric treated with melamine-formaldehyde resin. This difference can be attributed to the more rapid decomposition of the former as illustrated in Figure 21.

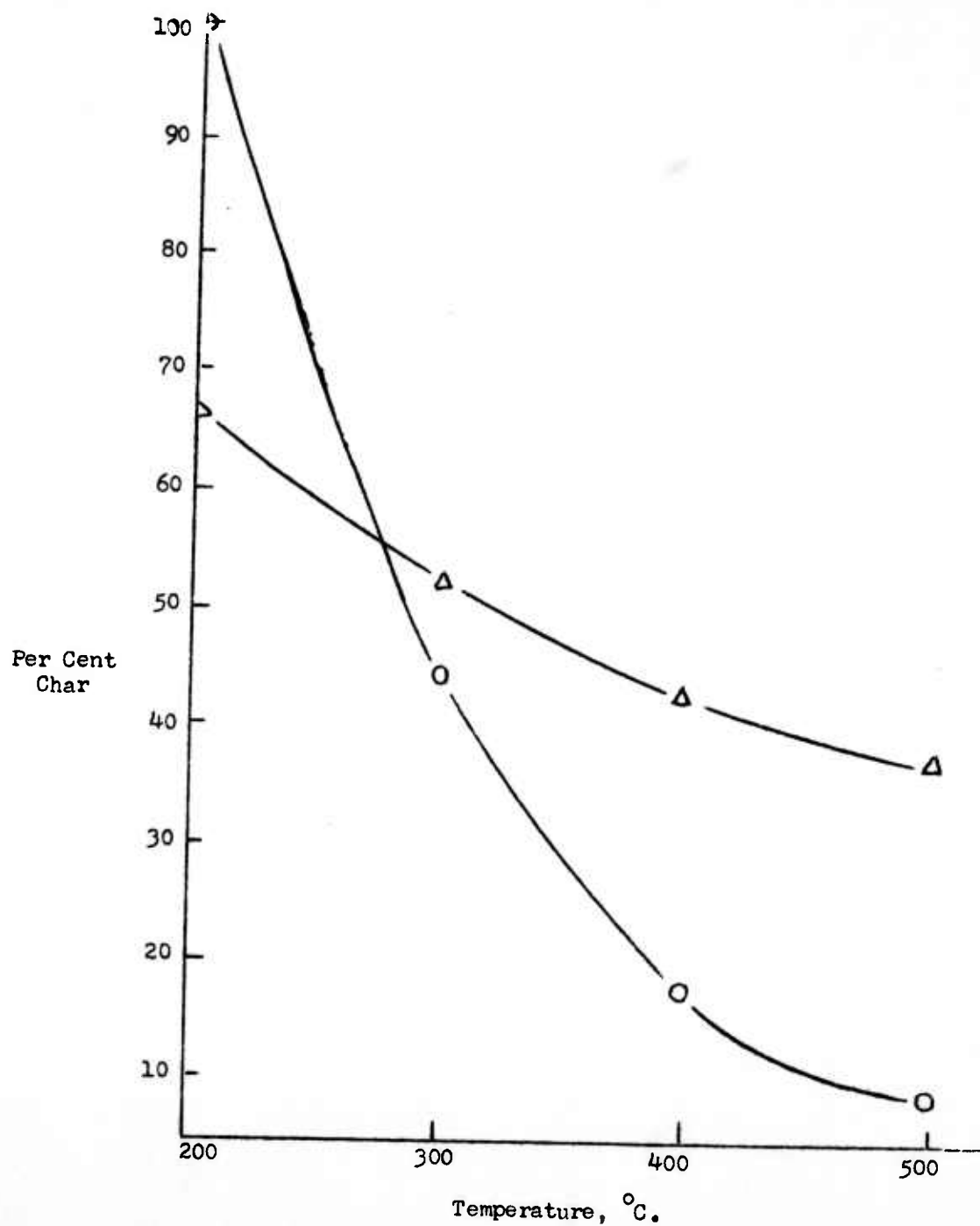


Figure 15. Pyrolysis of levoglucosan: untreated, O; 90% levoglucosan + 10%  $(\text{NH}_4)_2 \text{HPO}_4$ ,  $\Delta$ .

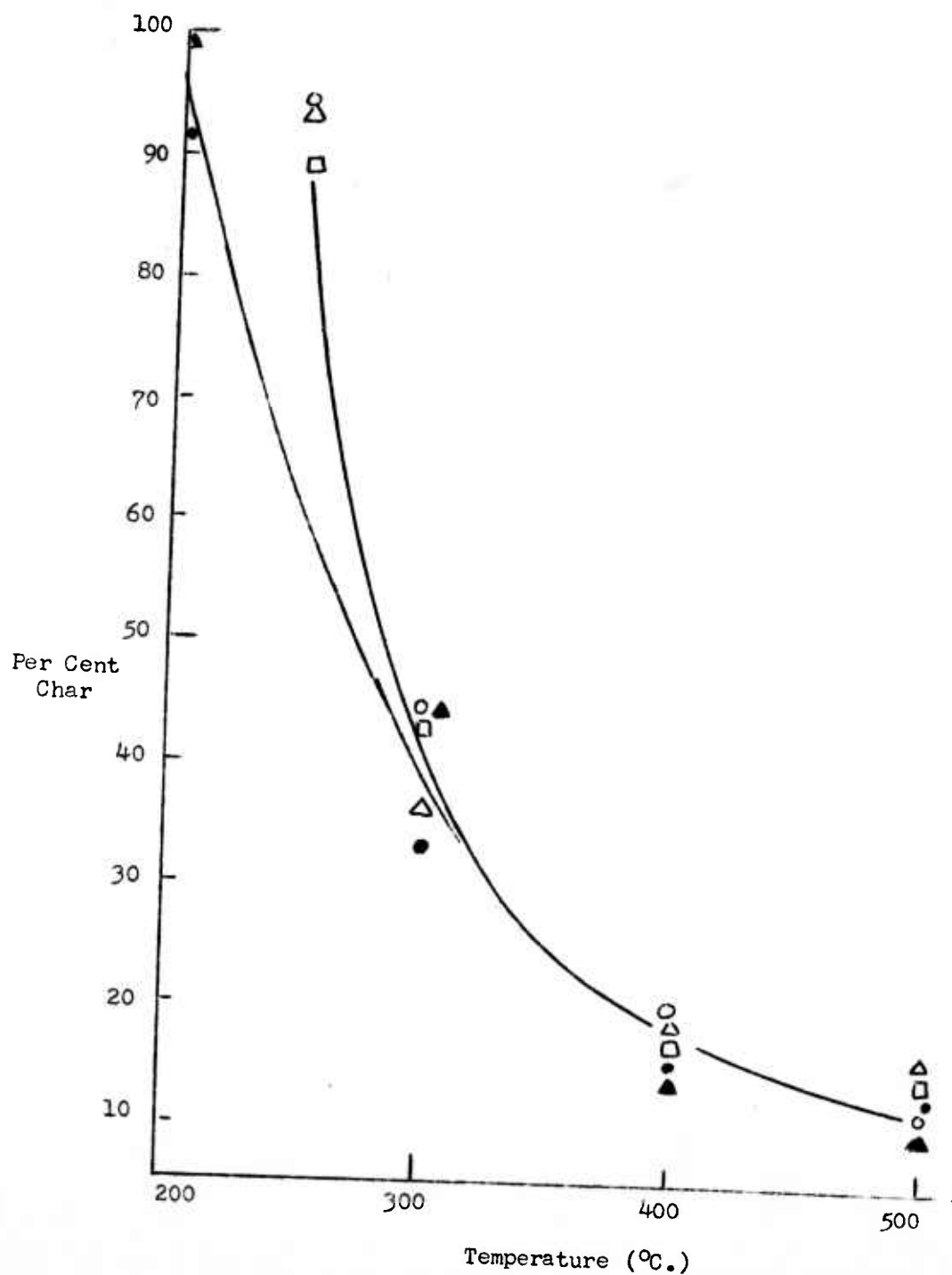


Figure 16. Pyrolysis of untreated cellulosic material: cotton fabric, O; rayon, Δ; hydrocellulose, □; glucose, ●; and levo-glucosan, ▲.

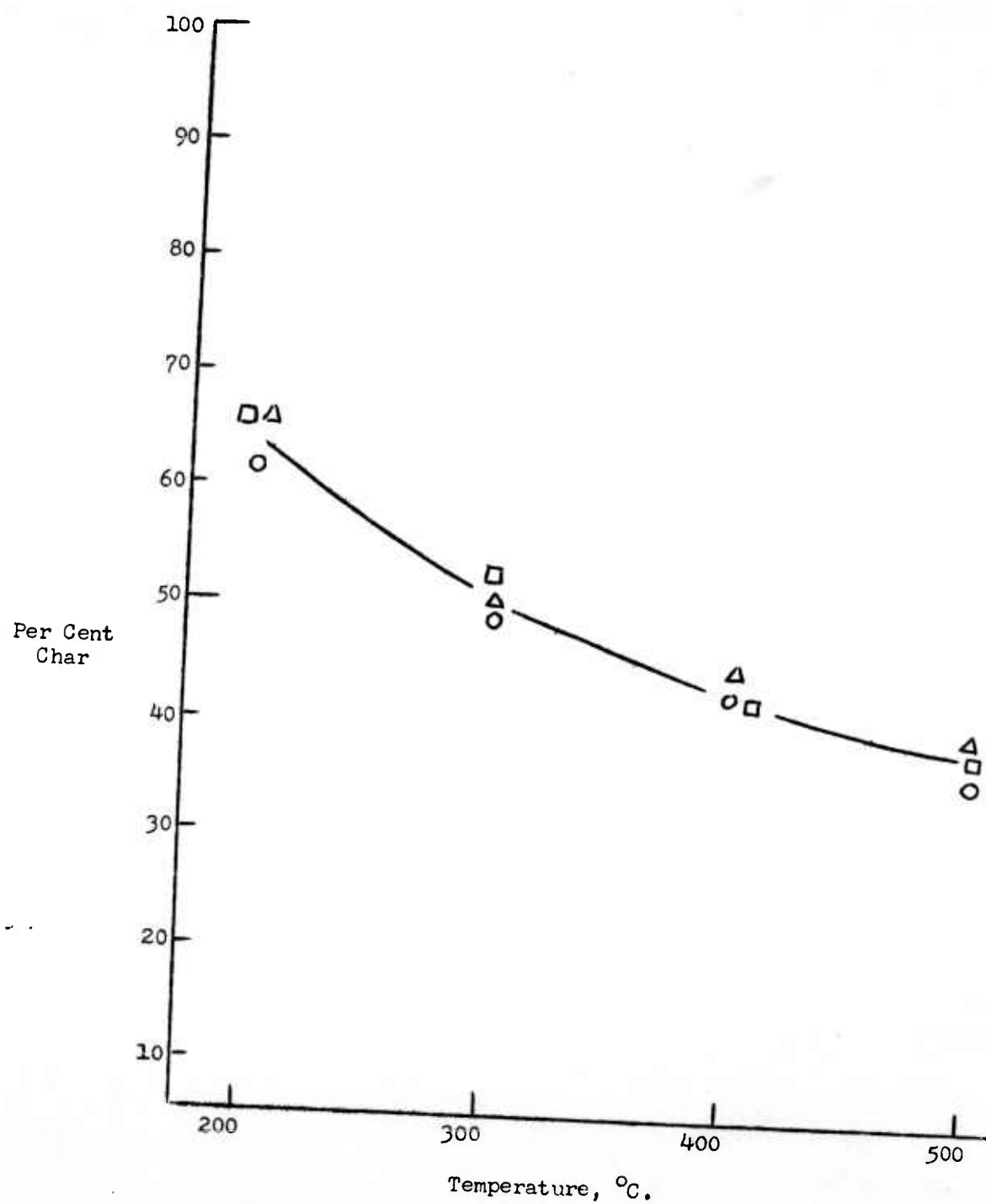


Figure 17. Pyrolysis of treated cellulosic materials: cotton + 9.2%  $(\text{NH}_4)_2 \text{HPO}_4$ ,  $\circ$ ; glucose + 10%  $(\text{NH}_4)_2 \text{HPO}_4$ ,  $\Delta$ ; levoglucosan + 10%  $(\text{NH}_4)_2 \text{HPO}_4$ ,  $\square$ .

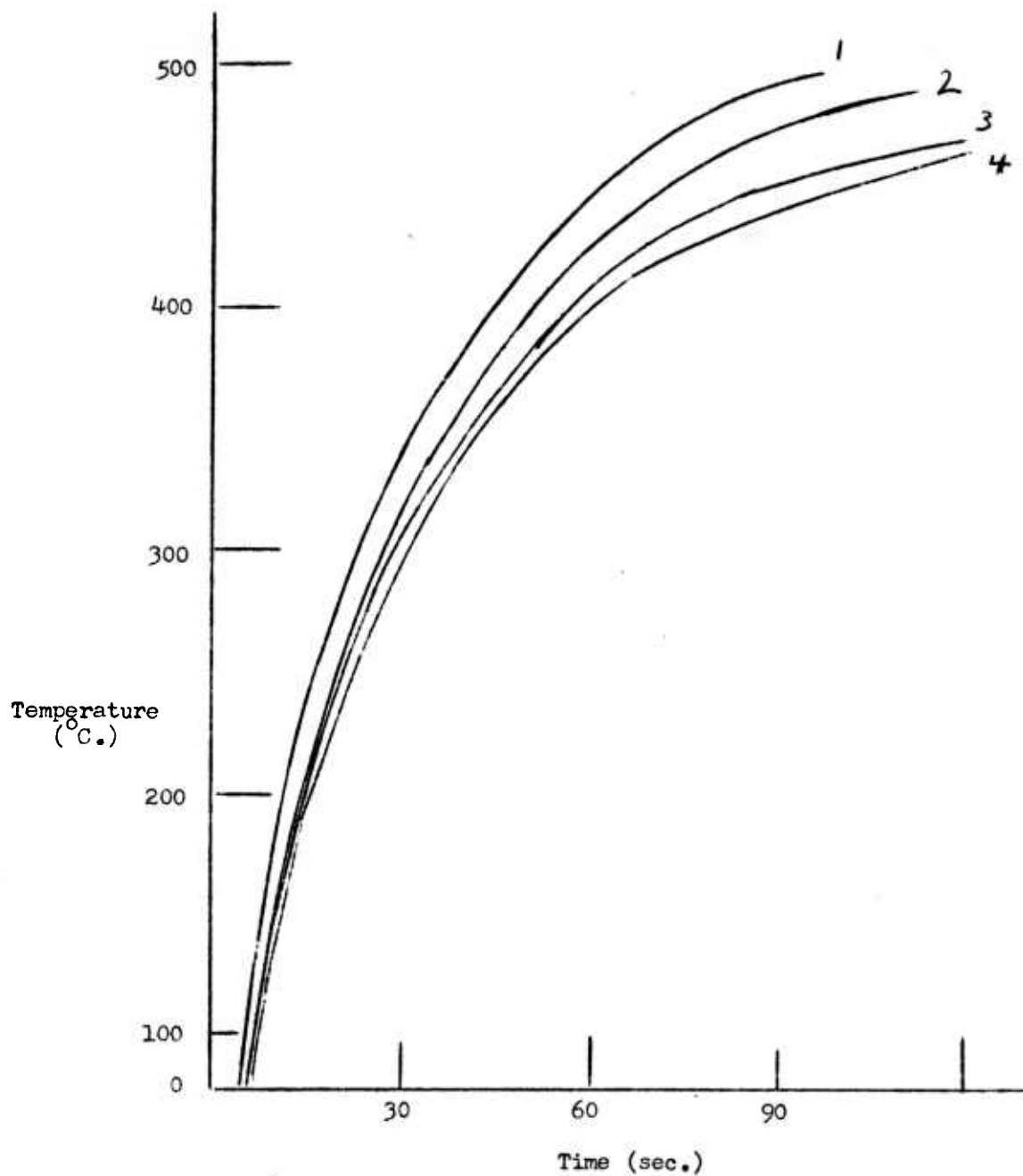


Figure 18. Relative insulation determination for cotton and melamine-formaldehyde treated cotton at 560° C. Variation of temperature with time by the hot plate method. Cotton fabric, 1; cotton fabric treated with 3.6% m-f, 2; 6.4% m-f, 3; and 15.2% m-f, 4.



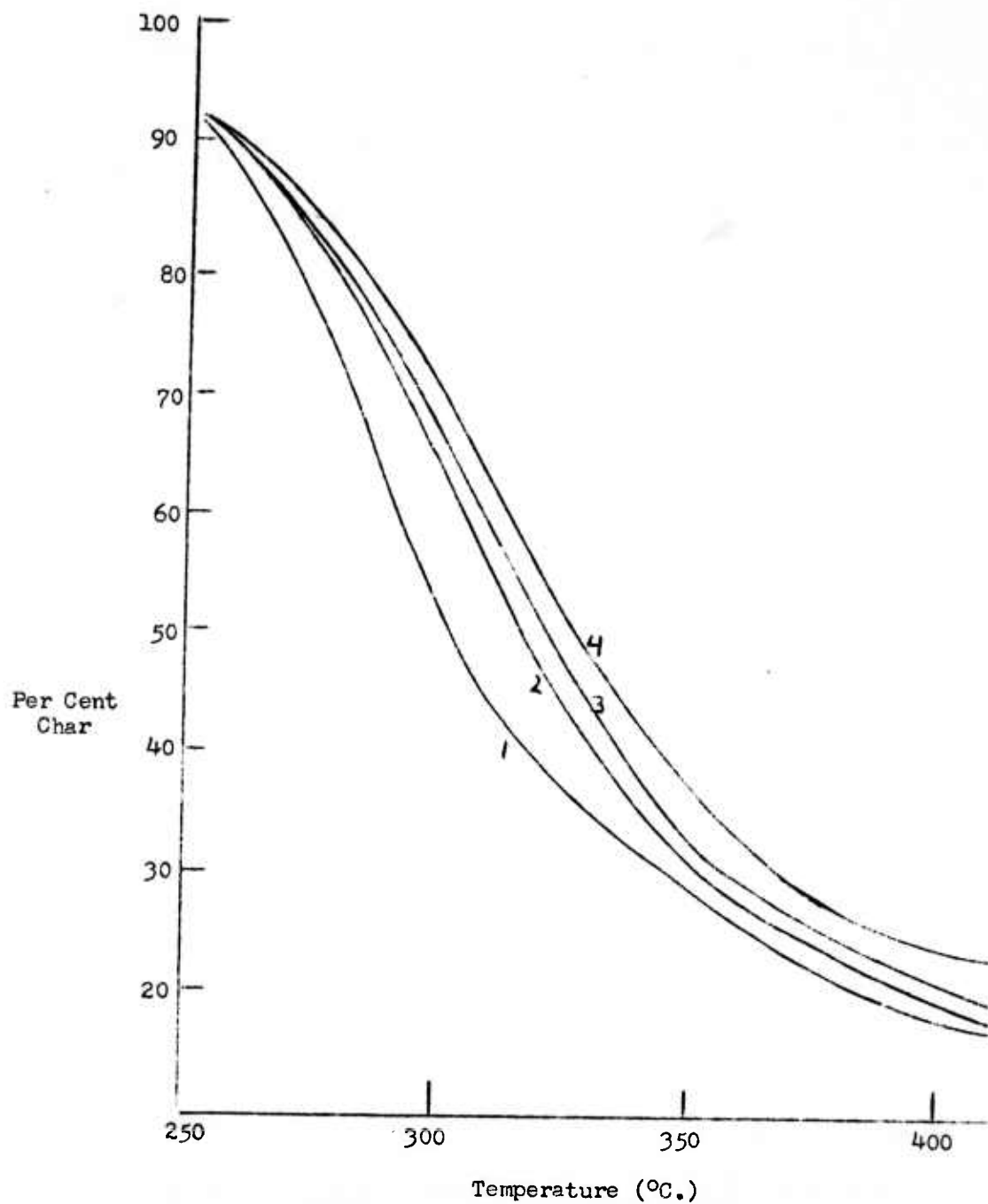


Figure 19. Variation of per cent char with temperature in the pyrolysis of cotton, 1; linen, 2; cotton treated with 1.6% melamine-formaldehyde resin, 3; and cotton treated with 6.4% melamine-formaldehyde resin, 4.

Rel. Heat Trans-  
mission at 560°C.  
for 2 min.

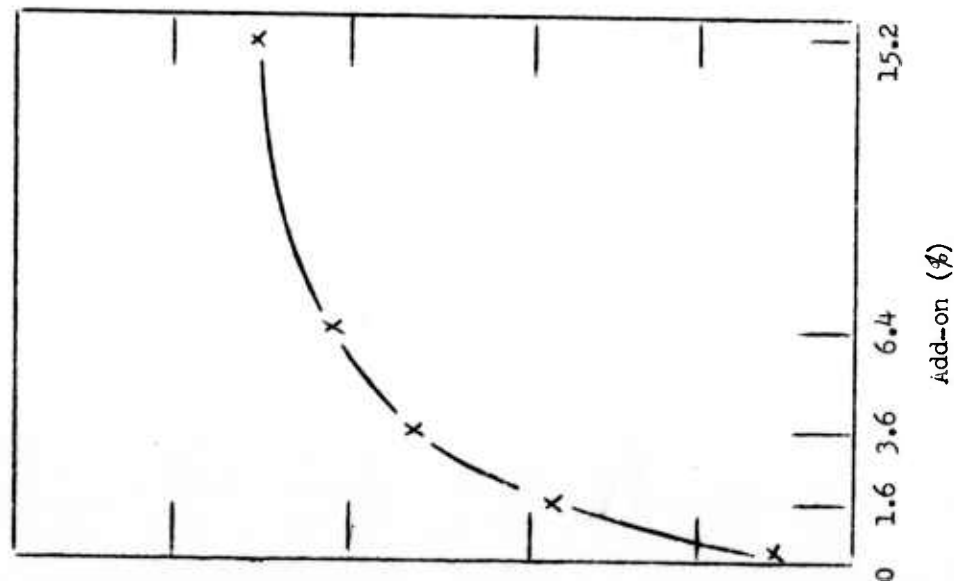


Figure 20A. Relative insulation afforded by cotton fabric and melamine formaldehyde treated cotton fabric to a hot plate at 560°C.

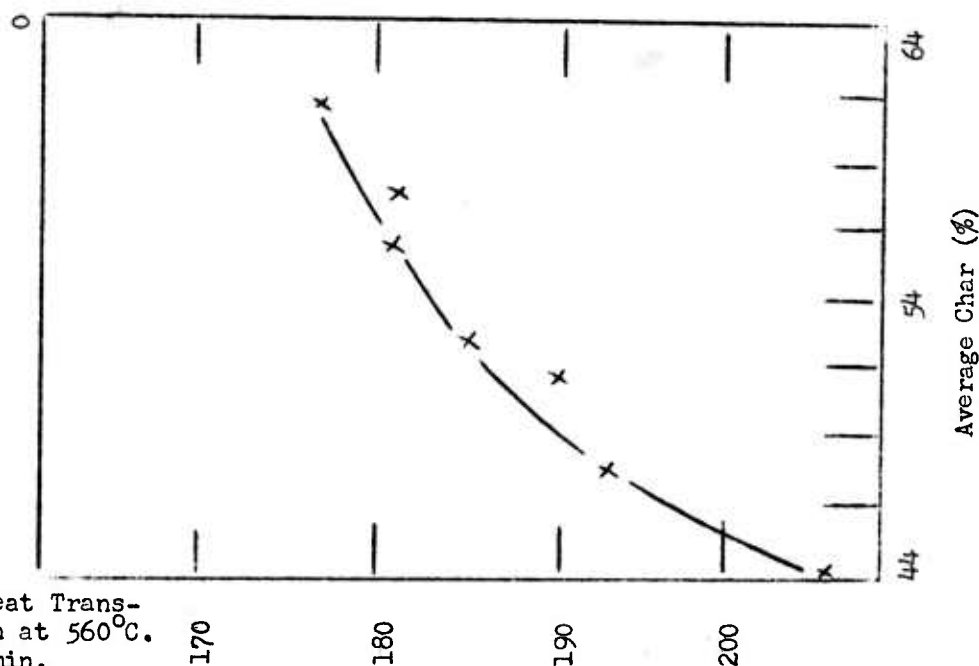


Figure 20B. Relation between the average char between 200-500°C. and insulation for cotton fabric, 1; and cotton fabric treated with melamine formaldehyde, 2-5 brompoly TAP, 6; Erifon, 7; and THPC, 8.

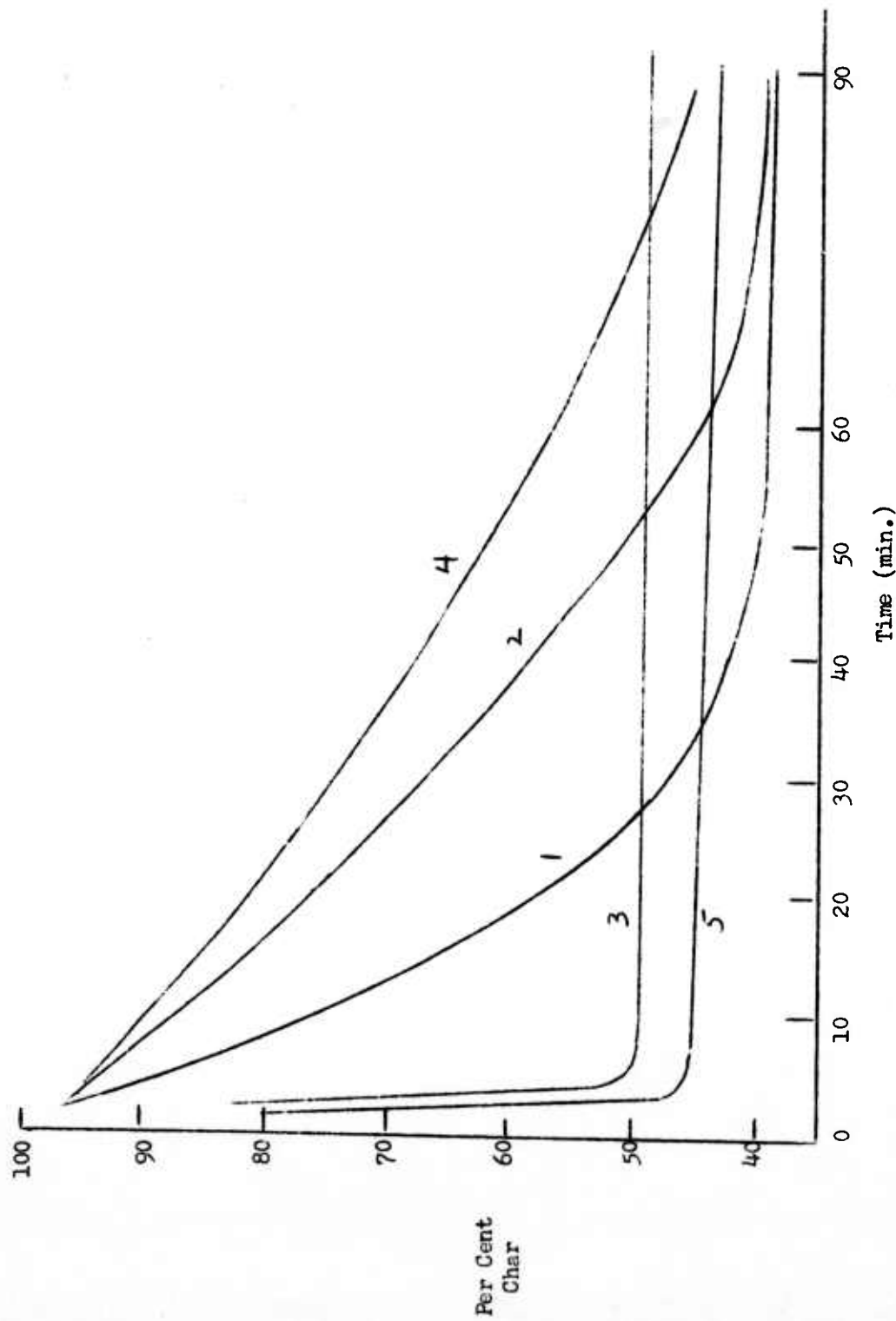


Figure 21.  
Rate of thermal decomposition at 325° C. of cotton, 1; linen, 2; cotton treated with 16% THPC-MF, 3; with 3.6% M-F, 4; and 10% Br-poly TAP, 5.

The insulation to heat provided by different cotton-wool blends was investigated. The variation of char with temperature is given in Figure 22A. The relative insulation up to 600, 700, and 800° C., or area under the char-temperature curves, is illustrated in Figure 22B in which the average char resulting at this temperature is plotted as a function of blend composition.

TABLE XI

Relative Insulation and Char for Untreated Cotton Fabric and Cotton Fabric Treated with Melamine-Formaldehyde Resin, Brominated Triallyl Phosphate Polymer, Erifon, and Tetrakis (hydroxymethyl phosphonium chloride).

| Fabric                         | Relative<br>Insulation<br>560° C. | Relative<br>Char area<br>from 200-500°C. | Relative<br>Insulation<br>600° C. | Relative<br>Char area<br>from 200-600°C. |
|--------------------------------|-----------------------------------|--|-----------------------------------|--|
| Untreated                      | 206                               | 161                                      | 263                               | 183                                      |
| 1.6% M-F <sup>a</sup>          | -                                 | 178                                      |                                   |  |
| 3.6% M-F                       | 184                               | 195                                      |                                   |  |
| 6.4% M-F                       | 179                               | 208                                      | 243                               | 230                                      |
| 15.2% M-F                      | 175                               | 230                                      |                                   |  |
| BromPoly TAP(19%) <sup>b</sup> | 190                               | 191                                      | 235                               | 236                                      |
| THPC <sup>c</sup> (16%)        | 180                               | 210                                      |                                   |  |
| Erifon (16%)                   | 180                               | 210                                      |                                   |  |

<sup>a</sup> Melamine-formaldehyde resin

<sup>b</sup> Brominated triallyl phosphate polymer

<sup>c</sup> Tetrakis- (Hydroxymethyl)-Phosphonium Chloride

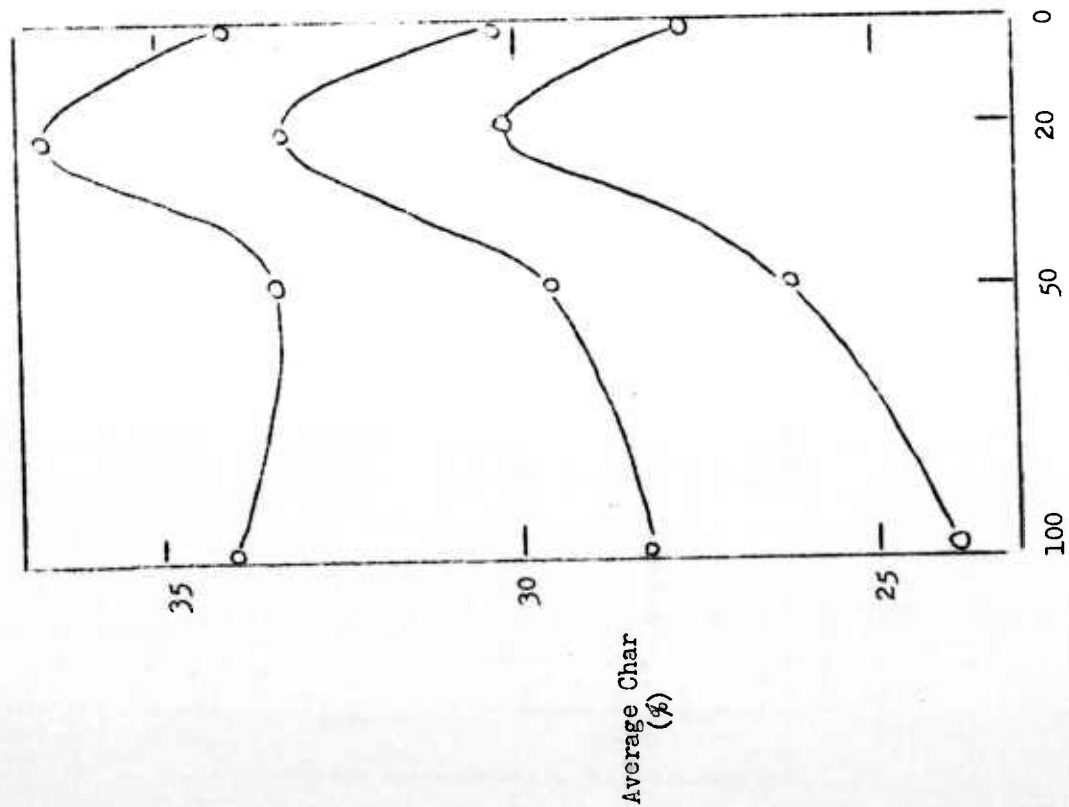


Figure 22A. Pyrolysis of cotton-wool blends. Total area under char-temp. plot as a function of blend composition.

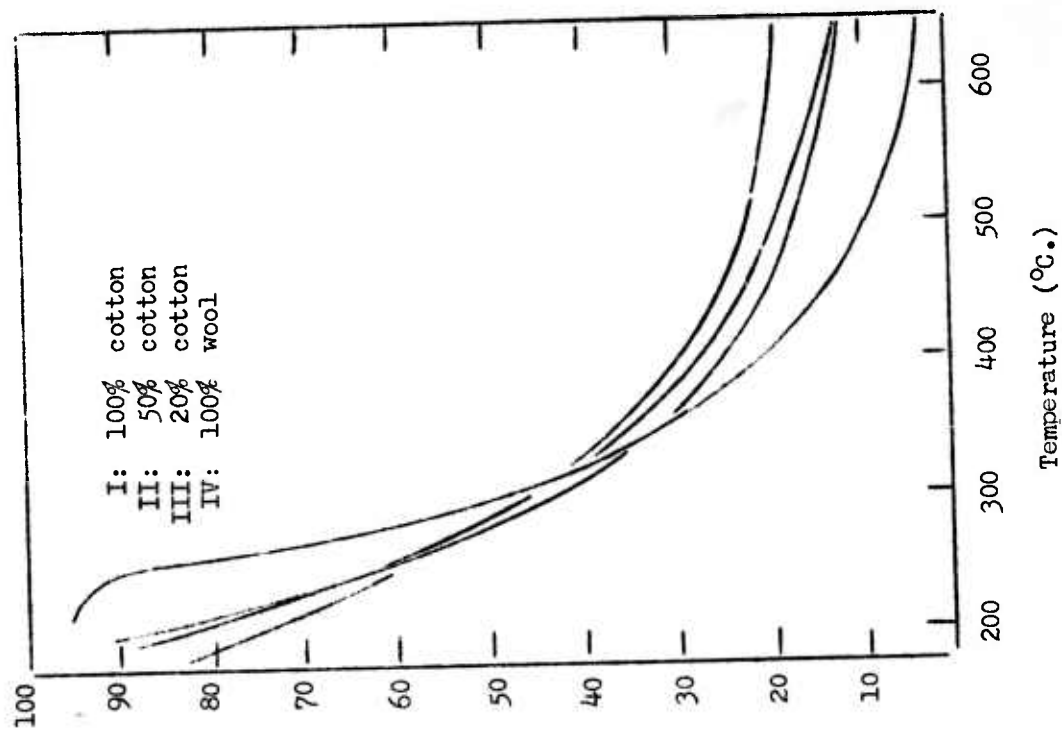


Fig. 5A. Pyrolysis of cotton, wool and cotton-wool blends.

### The Radiant Energy Decomposition of Cotton Fabric

The conventional methods used to study the thermal decomposition of untreated and treated cotton fabric (electric furnace) indicated a trend towards increased tar formation with increased rate of applied thermal energy and increased rate of decomposition. With the development of modern weapons the study of the exposure of cotton fabric to very rapid rates of incident energy was considered necessary. In order to overcome the limitations of the electric furnace in so far as rate of applied energy was concerned, this laboratory instituted an investigation of the decomposition of untreated and treated cotton fabric by radiant energy. A radiant source of energy, capable of a maximum irradiance of 9 - 10 cal.  $\text{cm}^{-2} \text{ sec}^{-1}$ , was used. The apparatus consisted of a 2,000 watt tungsten spotlight-type lamp with reflecting and condensing system, variable resistance and timer-controlled shutter mechanism.

A compact cell assembly, consisting of a Pyrex cell and sample holder, was designed and constructed for the exposure of fabric samples under pyrolytic and oxidative conditions. Since the output data of the instrument represented a spatial average of the irradiance (cal.  $\text{cm}^{-2} \text{ sec}^{-1}$ ) of a circular area of 1  $\text{cm}^2$  at the focal point of the source, the sample holder was designed to accommodate circular fabric samples small enough (0.95 cm. in diameter) to be totally exposed.

#### Preliminary Investigation and Modification of Apparatus.

Preliminary experiments failed to give reproducible results. For example, the per cent of char resulting from the exposure of single samples of untreated cotton khaki fabric at an irradiance of 7.7 cal.  $\text{cm}^{-2} \text{ sec}^{-1}$  for 5 seconds varied over a range of approximately 30 per cent.

The possible causes of the low precision were considered and investigated:

1. A low uniformity of fabric samples. A special punch and die assembly was constructed to provide uniform circular fabric samples (0.95cm. in diameter).
2. The very low weight of single samples. In order to overcome the large error inherent with the use of low weight single samples random sampling and the averaging of data from several experiments were adopted. For char investigations five circular samples were weighed together and exposed singly under the same conditions to constitute one determination. The average per cent of dried char from five such determinations constituted one exposure. The amount of tar resulting from an exposure (25 single samples) was determined from the increase in dry weight of the cell assembly.
3. Erratic timing mechanism causing variation in exposure time. In the investigation of possible causes of non-reproducibility a trend towards increased decomposition was observed during an exposure. The electronic timer supplied with the apparatus was checked against an electric synchronous motor-driven timer. The electronic timer was unsatisfactory.
4. Line voltage fluctuation causing variation in source output. A sensitive voltmeter, connected across the bulb terminals, did not reveal any appreciable voltage range for any voltage setting.
5. The condensation of tarry decomposition products on the cell window to decrease radiation intensity. In preliminary experiments the condensation of tarry products on the cell window was observed. Experiments were designed to determine whether this condensation interfered with the transmission of radiant energy. A series of exposures were completed in which the cell window was cleaned between determinations.

Comparison of the results of these experiments with those of exposures in which the cell window was not cleaned revealed no appreciable differences in per cent of char obtained.

6. Modification of apparatus to eliminate mechanical defects.

- a. The shutter assembly within the bulb housing was modified with aluminum shoes and rubber stops to prevent excessive vibration and jamming of shutter blade.
- b. During the operation of the radiant source apparatus the bulb housing was observed to become hot. Overheating of this unit could possibly cause expansion of the brass lens mount and a subsequent change in focal point of the apparatus. In order to eliminate overheating, the interior of the housing unit was painted with a white gloss heat-resistant paint; also the top vent of the unit was enlarged to provide a greater flow of cooling air from the attached blower.

During this phase of the investigation it was observed that test specimens from two different samples of cotton khaki fabric differed markedly in resistance to radiant energy. Under identical exposure conditions ( $3.3 \text{ cal. cm.}^{-2} \text{ sec.}^{-1}$  for 10 sec.) test specimens from one sample did not decompose (99% char) whereas test specimens of the second decomposed readily (63% char). This difference in behavior emphasized the necessity of using test specimens from the same sample of fabric for comparison studies.

These improvements and modifications of the apparatus produced an amount of char resulting from the exposure at infinite time of untreated and treated cotton khaki fabric, which varied within 11 per cent.



TABLE XII

Radiant Energy Decomposition of Untreated and Treated Cotton Khaki Fabric

| Sample   | Exposure<br>Experiment No. | Determination | % Char | Irradiance<br>( $\frac{\text{cal. cm.}^{-2}}{\text{sec.}^{-1}}$ ) | Time<br>(sec.) |
|--|----------------------------|---------------|--------|---|----------------|
| Untreated fabric   | 1                          | 1             | 13.7   | 5.3   | 8              |
|  |                            | 2             | 12.5   |   |                |
|  |                            | 3             | 13.0   |   |                |
|  |                            | 4             | 12.8   |   |                |
|  |                            | 5             | 14.0   |   |                |
|  | 2                          | 1             | 17.5   | 3.3   | 25             |
|  |                            | 2             | 17.7   |   |                |
|  |                            | 3             | 17.9   |   |                |
|  |                            | 4             | 17.2   |   |                |
|  |                            | 5             | 17.2   |   |                |
|  |                            | 1             | 24.2   | 7.7   | 5              |
|  |                            | 2             |        |   |                |
|  |                            | 3             |        |   |                |
|  |                            | 4             |        |   |                |
| Fabric treated with:<br>9.4% $(\text{NH}_4)_2\text{HPO}_4$ | 1                          | 1             | 29.1   | 5.3   | 8              |
|  |                            | 2             | 30.3   |   |                |
|  |                            | 3             | 29.9   |   |                |
|  |                            | 4             | 31.4   |   |                |
|  |                            | 5             | 29.3   |   |                |
|  |                            | 1             | 47.3   | 3.3   | 10             |
|  |                            | 2             | 47.3   |   |                |
|  |                            | 3             | 45.5   |   |                |
|  |                            | 4             | 43.8   |   |                |
| 16.3% THPC   | 1                          | 1             | 31.7   | 5.3   | 8              |
|  |                            | 2             | 28.7   |   |                |
|  |                            | 3             | 28.5   |   |                |
|  |                            | 4             | 27.7   |   |                |
|  |                            | 5             | 25.7   |   |                |
| 6.1% Br poly TAP   | 1                          | 1             | 45.9   | 3.3   | 11             |
|  |                            | 2             | 43.4   |   |                |
|  |                            | 3             | 47.1   |   |                |
|  |                            | 4             | 43.9   |   |                |
|  |                            | 5             | 42.8   |   |                |
| 18.3% Br poly TAP  | 1                          | 1             | 17.8   | 5.3   | 8              |
|  |                            | 2             | 18.2   |   |                |
|  |                            | 3             | 18.3   |   |                |
|  |                            | 4             | 18.6   |   |                |
|  |                            | 5             | 18.3   |   |                |
|  | 2                          | 1             | 62.1   | 3.3   | 10             |
|  |                            | 2             | 60.8   |   |                |
|  |                            | 3             | 60.9   |   |                |
|  |                            | 4             | 60.2   |   |                |

The effect of radiant energy on untreated 80 square cotton fabric was studied. This fabric offered a much greater resistance to decomposition than was observed for untreated cotton khaki fabric. This difference in behavior undoubtedly results from the wide variation in reflectance properties of both fabrics.

TABLE XIII

Comparison of Radiant Energy Decomposition of  
Untreated 80 Square Cotton Fabric with  
Untreated Cotton Khaki Fabric

| Sample                     | Exposure<br>Experiment No. | % Char<br>(ave.) | Irradiance<br>(cal.cm. <sup>-2</sup> sec. <sup>-1</sup> ) | Time<br>(sec.) - |
|----------------------------|----------------------------|------------------|---|------------------|
| 80 Square<br>Cotton fabric | 1                          | 98               |   |                  |
|                            | 2                          | 97               | 7.7   | 11               |
|                            | 3                          | 95               | 7.7   | 13               |
|                            | 4                          | 65               | 7.7   | 14               |
| Cotton khaki               |                            |                  | 7.7   | 18               |
|                            | 1                          | 17.5             | 3.3   | 25               |
|                            | 2                          | 13.2             | 5.3   | 8                |
|                            | 3                          | 12.4             | 7.7   | 5                |

Experiments were started on a comparison of the radiant energy decomposition of untreated and treated cotton khaki fabric with the thermal decomposition of the same fabrics (electric furnace) at different rates. In all cases pyrolytic conditions were maintained, and the decompositions position carried out to infinite time. As shown in the following table, an increased rate of incident energy on the samples produced larger quantities of tars.

TABLE XIV

Effect of Varying Rates of Thermal Decomposition of Cotton Khaki Fabric on the Amount of Char and Tar Produced

| Sample  | Char/Tar Ratio        |                   |  |                   |      |
|---|-----------------------|-------------------|--|-------------------|------|
|   | Furnace Block Decomp. |                   | Radiant Energy Decomp.                                 |                   |      |
|   | 400° C.               | 500° C.           | (5.3 cal.cm. <sup>-2</sup> sec. <sup>-1</sup> for 8sec |                   |      |
|   | Slow <sup>a</sup>     | Fast <sup>b</sup> | Slow <sup>a</sup>                                      | Fast <sup>b</sup> |      |
| Untreated fabric                                      | 0.45                  | 0.36              | 0.49   | 0.23              | 0.35 |
| Fabric treated with:                                  |                       |                   |  |                   |      |
| 9.2% (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> | 3.93                  | 2.57              | 2.96   | 2.24              | 1.27 |
| 16% THPC  | 3.90                  | 2.54              | 3.50   | 2.12              | 0.88 |
| 19.2% Br poly<br>TAP                                  | 2.09                  | 1.58              | 1.88   | 1.18              | 0.48 |

#### Spectral Response of the Tungsten Lamp.

The spectral distribution of the tungsten lamp was measured with a Perkin-Elmer Double Pass Monochromator, Model 99, Serial 8, equipped with a sodium chloride prism. The output was amplified and rectified by means of a Perkin-Elmer Narrow Band Amplifier, Model 107, and recorded on a Leeds and Northrup Speedomax, Type G.

The spectral response was determined for bulb voltage inputs of 30-100 v. The wavelength range of the radiation output was 0.75 - 2.2 $\mu$

Energy was not obtained at wavelengths greater than 2.2 $\mu$  because of the absorbing properties of the condensing lens system. A negligible variation in maximum radiation wavelength (1.34 - 1.43 $\mu$ ) indicated a relatively constant black body temperature of the source within the limits of applied bulb voltages (30-100v.).

#### Temperature Measurement.

An apparatus for the measurement of temperature behind fabric samples during exposure to the radiant energy is under construction. A rapid response thermocouple with a time constant of approximately 25 milliseconds has been prepared from one mil platinum-rhodium and gold-palladium wire<sup>a</sup>. The thermocouple will be incorporated in a Teflon mount. The Pyrex cell will be modified to accommodate the thermocouple housing. A Brown Electronik Recorder will be used to record the e. m. f. produced at the thermocouple by the heat behind fabric samples.

#### Experimental.

Circular samples of fabric were dried over anhydrous calcium chloride for at least 24 hours. The dried samples were weighed in groups of five<sup>b</sup>.

<sup>a</sup> The thermocouple was obtained from the Eppley Laboratories, Newport, R.I.

<sup>b</sup> A group of five samples weighed together and exposed singly under identical conditions constituted one determination. Five such determinations represented one exposure.

A single fabric sample was mounted on the dry, previously weighed sample holder with the aid of a specially constructed jig assembly. The holder was then placed within the dry, previously weighed Pyrex cell. Exposure to radiation was completed under an atmosphere of dry nitrogen. The per cent of char was determined from the average dry weight of residue resulting from five determinations (one exposure). The amount of tar was determined by the net gain in dry weight of the cell assembly after an exposure.

R E F E R E N C E S

1. J. H. Baxendale, M. G. Evans and G. S. Parks, Trans. Faraday Soc., 42, 155 (1946).
2. J. D. Guthrie, J. D. Reid and coworkers, "Development of Durably Flameproofed Textiles for Military Use," Southern Regional Research Laboratory, U. S. Dept. of Agriculture, New Orleans, La., Progress Report No. VI, Quartermaster Project No. 7-92-06-001, Dec. 31, 1952.
3. M. S. Kharasch, et al., J. Am. Chem. Soc., 69 1100, 1105 (1947); J. Org. Chem., 13, 895 (1948); ibid., 14, 537 (1949).
4. J. D. Reid and coworkers, "Mechanism of Flameproofing Cotton by Means of Halogenated Phosphate Polymers," Southern Regional Research Laboratory, U. S. Dept. of Agriculture, New Orleans, La., Progress Report No. II, Quartermaster Project No. 7-92-06-001, Dec. 31, 1951.
5. H. C. Speel, "Textile Chemicals and Auxiliaries", Reinhold Publishing Corp., New York, N. Y., 1952, p. 111.
6. Reference 5, p. 405.
7. J. M. Church, "Fundamental Studies of Chemical Retardants for the Fire Resistant Treatment of Textiles," Textile Series Report No. 38, Office of the Quartermaster General, Department of the Army, 1952, p. 276.
8. H. Bestian, Ann., 566, 210 (1950).
9. R. W. Little, "Flameproofing Textile Fabrics," Reinhold Publishing Corp., New York, N. Y., 1947.
10. Reference 7, pp. 12-14.
11. C. D. Hurd, "The Pyrolysis of Carbon Compounds," The Chemical Catalog Company, Inc., New York, N. Y., 1929, pp. 278-283.
12. E. Heuser, "The Chemistry of Cellulose," John Wiley and Sons, Inc., New York, N.Y., 1944, pp. 545-554.

13. Reference 7, pp. 7-21.
14. Reference 9, pp. 43-46.
15. Reference 7, pp. 22-53.
16. Reference 9, pp. 41-76.
17. Reference 7, p. 74.
18. K. Tamaru, Bull. Chem. Soc. Japan, 24, 164 (1951).
19. A. Pictet and J. Sarasin, Helv. Chim. Acta, 1, 87 (1918).
20. E. M. Chamot and C. W. Mason, "Handbook of Chemical Microscopy," Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 458.
21. R. E. Wagner and E. Pacsu, Textile Research J., 22, 12 (1952).
22. A. E. Knauf, R. M. Hahn and C. S. Hudson, J. Am. Chem. Soc., 63, 1447 (1941).
23. R. M. Hahn and C. S. Hudson, ibid., 64, 2435 (1942).
24. H. J. P. Venn, J. Textile Inst., 15, T414 (1924).